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## THE CHEMISTRY OF ETHYLENE OXIDE

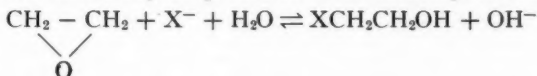
### V. THE REACTION OF ETHYLENE OXIDE WITH HALIDE IONS IN NEUTRAL AND ACID SOLUTION<sup>1</sup>

By A. M. EASTHAM AND G. A. LATREMOUILLE

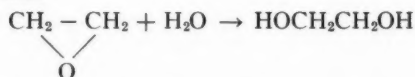
#### ABSTRACT

The rates of reaction of halide ions with ethylene oxide in neutral aqueous solution and the rate of hydrolysis of ethylene oxide in acid solution have been measured and the activation energies determined. From these data and from the ratio of glycol to chlorohydrin formed when ethylene oxide reacts with excess aqueous hydrogen halide, the rates of the acid-catalyzed addition of halide ions to ethylene oxide at 25°C. have been estimated.

In aqueous solution ethylene oxide reacts with halide ions to form halo-hydrins. These reactions were studied for a number of substituted oxides at 20°C. by Bronsted, Kilpatrick, and Kilpatrick (1) and shown to occur by both uncatalyzed and acid-catalyzed processes. The uncatalyzed reactions



were followed by measuring the rate of acid addition required to keep the solution neutral and were usually sufficiently rapid that the uncatalyzed hydrolysis of the oxide



did not seriously interfere with the measurements. In acid solution, however, the formation of glycol was an important side reaction and the accurate measurement of the rate of the acid-catalyzed addition of halide ions was therefore difficult. Bronsted *et al.* succeeded in making such measurements for the bromide-glycid system by measuring the rate of change in the conductivity of the solution, and established that the reaction was of the third order, dependent upon the oxide, hydrogen ion, and bromide ion concentrations. The method was laborious and was therefore applied only to the one reaction, but the authors did record some approximate rate constants for the acid-catalyzed addition of chloride and bromide ions to ethylene oxide.

In the course of work in these laboratories it became desirable to extend some of these data to ethylene oxide itself and accordingly, the uncatalyzed

<sup>1</sup> Manuscript received September 17, 1951.

Contribution from the Division of Chemistry (Applied), National Research Council. Issued as N.R.C. No. 2634.

rates of halide ion addition were measured, using a slight modification of Bronsted's method. The rates were sufficiently slow to suggest that an estimate of the acid-catalyzed rates could be made by measuring the ratio of glycol to chlorohydrin formed from ethylene oxide in a large excess of acid. This ratio, as pointed out by Lichtenstein and Twigg (5) is expressed approximately by the equation

$$\frac{\text{Glycol}}{\text{Chlorohydrin}} = \frac{k_1}{k_2} (X^-)$$

where  $k_1$  and  $k_2$  are the rate constants for the acid-catalyzed formation of glycol and of halohydrin respectively and where  $(X^-)$  is the concentration of halide ion. The value of  $k_1$  may be determined independently and therefore by using a large excess of halide ion to minimize concentration changes, the value of  $k_2$  may be estimated from the glycol/halohydrin ratio, on the assumption that these are the only products formed.

#### EXPERIMENTAL

(a) The rates of the uncatalyzed addition of halide ions to ethylene oxide were determined as follows. A four-necked flask fitted with a mechanical stirrer, a 5 ml. burette and the external electrodes of a Beckman model G pH meter was held in a constant temperature bath regulated to 0.01°C. The burette was graduated in units of 0.01 cc. and was tipped with a small stainless steel hypodermic needle to permit the addition of very small drops of liquid. A solution of alkali metal halide was adjusted to pH 7.0 with the corresponding acid and a known volume introduced into the flask and allowed to come to bath temperature. A weighed ampoule of ethylene oxide was broken under the solution, the stirrer started, and acid was then added from the burette at such a rate that the pH of the solution was kept between 6 and 8. Measurements were made only in the first 5% of reaction and the concentration of acid was so adjusted that the increase in volume of the solution during the period of measurement was not over 2%. The chloride and bromide reactions were titrated with the corresponding acids and calculated as pseudo-first order reactions but, because of the instability of hydrogen iodide, the rate of iodide addition was followed with perchloric acid and calculated by second order methods. Sodium perchlorate was used as a neutral salt in the determination of salt effects.

(b) The rate of the acid-catalyzed hydrolysis of ethylene oxide was determined dilatometrically according to the method of Bronsted *et al.* and corrected for the uncatalyzed reaction by means of the data of Lichtenstein and Twigg (5).

(c) The ratio of glycol to chlorohydrin formed in the reaction of ethylene oxide with acid solutions of halide ions was determined by the following procedure. A weighed sample of ethylene oxide was broken into a hydrogen halide-sodium halide solution of known volume and concentration and allowed to react completely; the initial halide ion concentration of the solution was always at least 10 times that of the ethylene oxide but the hydrogen ion



concentration was varied from about 2 to 10 times that of the oxide. The reaction mixture was then analyzed for halohydrin by acid-base titration or for glycol by periodate oxidation, or both, using methods very similar to those previously described (3). The analyses were carefully tested on synthetic mixtures of acid, glycol, and halohydrin before use. No difficulty was experienced with chloride mixtures and bromides gave good results when procedures were standardized and blanks carefully determined. The determination of glycol in the iodide solutions by means of periodate, however, was only accomplished after first precipitating the excess iodide with silver nitrate and then rapidly removing the excess silver with sodium chloride; under these conditions, reproducible and apparently accurate analyses were obtained.

No appreciable amount of free iodine was liberated during the reaction of oxide with the iodide. Reactions with hydrofluoric acid were conducted in polystyrene containers.

The glycol/chlorohydrin ratios as determined by glycol analysis were in reasonable agreement with those obtained by acid-base titration at the lower halide concentrations but above about 0.5 molar discrepancies were observed (Fig. 7). The deviations may have been due to the formation of polymeric products such as diethylene glycol, etc. Altering the  $HX/NaX$  ratio did not appear to influence the deviation. Measurements were made at 25° and at 0° but the ratios were not sufficiently sensitive to temperature to permit an estimate of the activation energies. The data were plotted (Fig. 7) and the rate constants estimated from the smoothed curve.

#### RESULTS

The rates for the uncatalyzed addition of halide ions to ethylene oxide are shown in Figs. 1, 2, 3, and the activation energies for these reactions are shown in Fig. 4. In estimating the activation energies, rates were compared at a concentration of halide ions common to the three temperatures rather than at zero concentration to avoid extrapolation errors.

It is perhaps of interest to note that lithium chloride seems to give a positive salt effect whereas sodium chloride gives the usual negative salt effect in these reactions (Fig. 1). This difference may simply be due to the fact that the activity of lithium chloride increases while that of sodium chloride decreases in the concentration range of these experiments. It is however of interest to note that some recent experiments (to be published) in pyridine solution have led us to believe that lithium ions may indeed have some catalytic activity towards ethylene oxide reactions.

Figs. 5 and 6 show the rates, salt effects, and activation energy for the acid-catalyzed hydrolysis of ethylene oxide. The data appear to be in good agreement with those of Bronsted *et al.*

Fig. 7 shows the ratio of glycol to halohydrin obtained when ethylene oxide is allowed to react with acid solutions of halide ions. From the smoothed curves the acid-catalyzed rate constants were calculated and are shown in Table I; it is evident that the bromide and iodide constants show a consider-

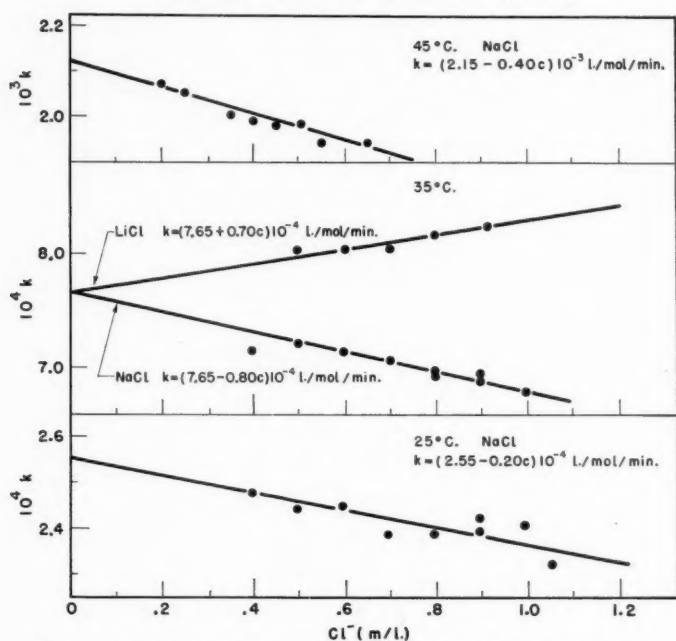


Fig. 1. Reaction of ethylene oxide with chloride ion in neutral solution.

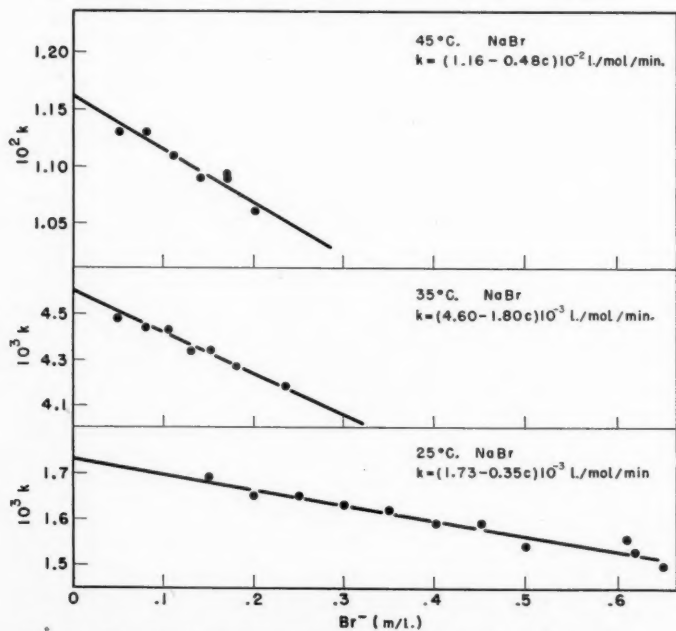


Fig. 2. Reaction of ethylene oxide with bromide ion in neutral solution.

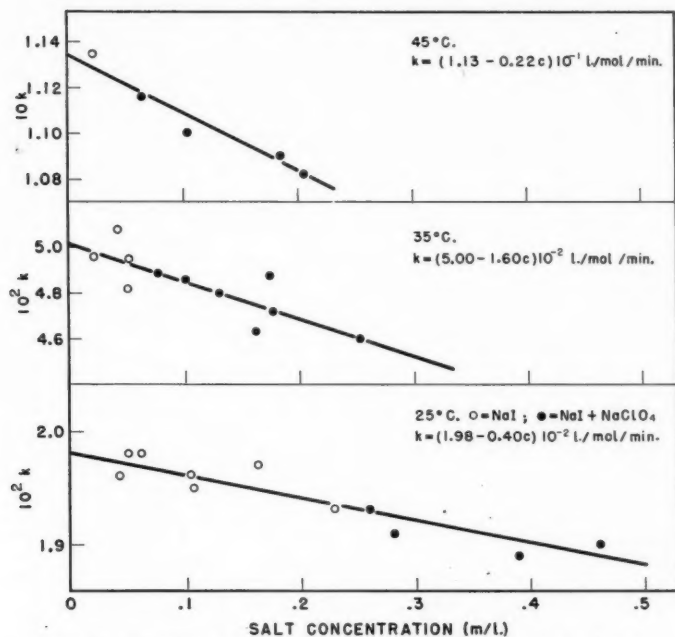


Fig. 3. Reaction of ethylene oxide with iodide ion in neutral solution.

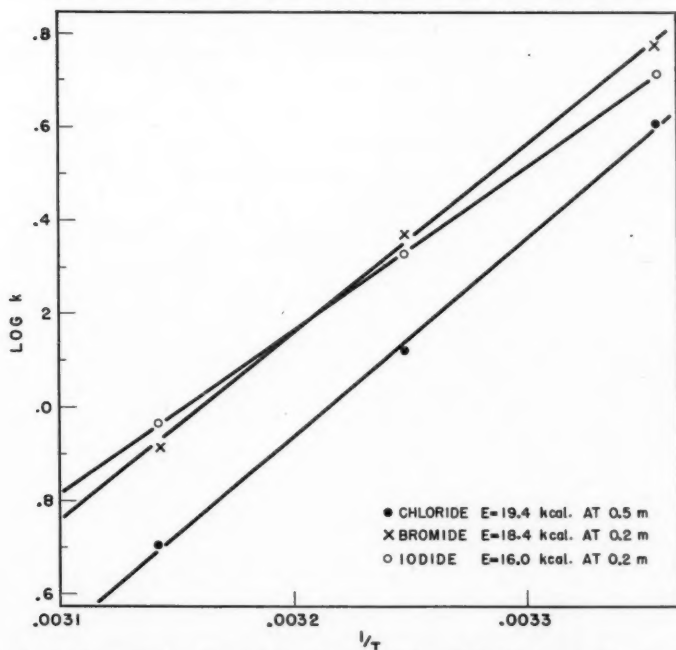


Fig. 4. Activation energies for the uncatalyzed addition of halide ions to ethylene oxide.

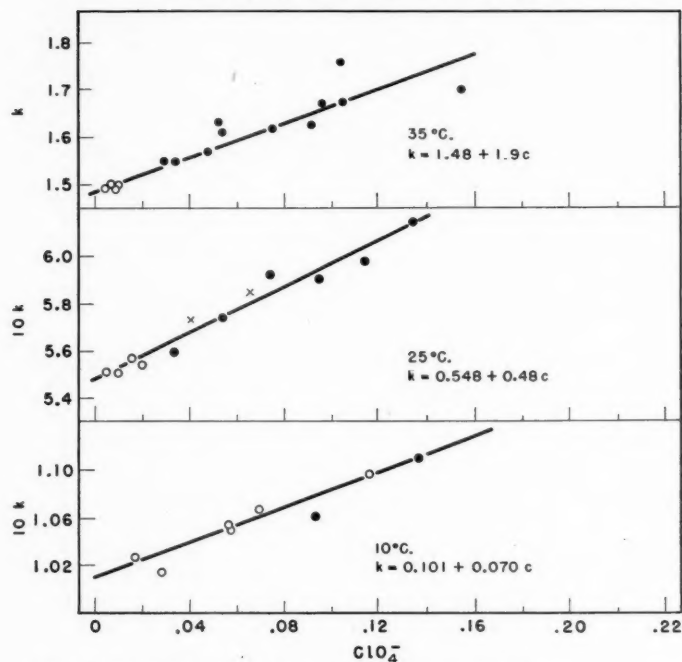


Fig. 5. The acid-catalyzed hydrolysis of ethylene oxide.  
 $\circ = \text{HClO}_4$  alone;  $\bullet = \text{HClO}_4 + \text{NaClO}_4$ ;  $\times = \text{HClO}_4 + \text{LiClO}_4$ .

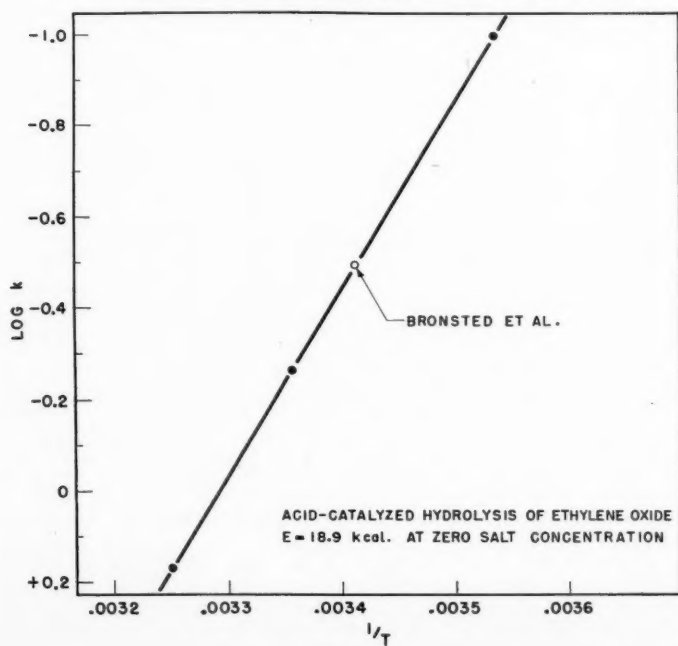


Fig. 6.

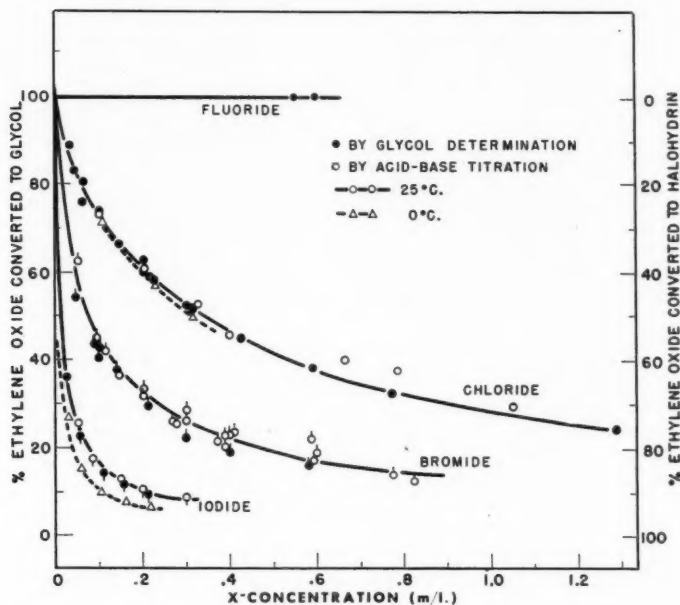


Fig. 7.

able drift towards lower rates as the concentration increases and the recorded average values must therefore be regarded as very approximate. The approximate values reported by Bronsted *et al.* are included for comparison.

The results of all these experiments, together with the corresponding data for a number of other reactions of ethylene oxide, are shown in Table II.

TABLE I

Halide ion concentration, moles per liter	$k_H^+$ at 25° for the formation of:			
	Glycol (l.mol. <sup>-1</sup> min. <sup>-1</sup> )	Chlorohydrin	Bromohydrin (l. <sup>2</sup> mol. <sup>-2</sup> min. <sup>-1</sup> )	Iodohydrin
.025	0.56			37
.050	0.57	2.5		34
.075	0.58	2.4	7.7	33
.10	0.60	2.3	7.5	32
.15	0.62	2.2	7.1	29
.20	0.64	2.1	6.8	30
.30	0.69	2.1	6.9	
.40	0.74	2.1	6.6	
.50	0.79	2.2		
Average		2.2	7.0	33
Bronsted <i>et al.</i>		2.2	8.7	

TABLE II

Reagent	Temp.	Uncatalyzed		Acid-catalyzed	
		$k$ (l.mol. <sup>-1</sup> min. <sup>-1</sup> )	Activation energy (kcal.)	$k_{H^+}$ (l. <sup>2</sup> mol. <sup>-2</sup> min. <sup>-1</sup> )	Activation energy (kcal.)
I <sup>-</sup>	25°	$2.0 \times 10^{-2}$	16.0	33	
Br <sup>-</sup>	"	$1.7 \times 10^{-3}$	18.4	7.0	
Cl <sup>-</sup>	"	$2.5 \times 10^{-4}$	19.4	2.2	
F <sup>-</sup>	"			Very small	
OH <sup>-*</sup>	"	$6.7 \times 10^{-3}$	18.1		
H <sub>2</sub> O**	"	$7.3 \times 10^{-7}$	19.0*	.010	18.9
Most amines†	"	$10^{-1}$ to $10^{-3}$			
NH <sub>3</sub> ††	"	$8.2 \times 10^{-3}$	14.6		

\* Lichtenstein and Twigg (5).

\*\* The experimentally determined rate constants for the hydrolysis reactions have been divided by the concentration of water (55.5 moles per liter) in order to give them the same dimensions as the other constants.

† Eastham et al. (2).

†† Ferrero et al. (4).

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## CHARCOAL SORPTION STUDIES

### I. THE PORE DISTRIBUTION IN ACTIVATED CHARCOALS<sup>1</sup>

By H. L. McDERMOT AND J. C. ARNELL

#### ABSTRACT

The pore distributions of three activated charcoals have been calculated from the low temperature nitrogen and water isotherms. The method of Barrett, Joyner, and Halenda has been used with the nitrogen data, while the Kelvin equation has been applied to the water isotherm. The two curves coincide if  $\cos \theta = 0.65$  is used in the Kelvin equation, where  $\theta$  is the wetting angle. This figure is in general agreement with a published figure obtained by an independent method.

#### INTRODUCTION

The determination of the pore size distribution of an activated charcoal is one of considerable practical importance. The success of any chemical impregnation depends to a large extent on the existence of pores of certain diameters. Also, pore size measurements can be used to indicate the progress of activation of a base char by steam or gas.

Several methods have been used to measure these distributions of pore sizes. Making the assumption that the desorption side of the hysteresis loop of a water isotherm on activated charcoal results from the evaporation of water condensed in pores of the charcoal, it is possible to calculate the pore distribution from the Kelvin equation (4). A second method involves the measurement of the surface areas of charcoals equilibrated with varying quantities of water and calculating the pore radius from the equation

$$r = \frac{2V}{A},$$

where  $r$  = the average pore volume between volume increments of water sorbed,

$V$  = the volume of the unfilled pores, and

$A$  = the surface area of the unfilled pores (4).

It is necessary to know the total pore volume of the charcoal filled with water at saturation. A more recent method, which only gives the distribution of the larger pores, not easily measured by the other two methods, makes use of a mercury porosimeter (6). With this apparatus, it is possible to determine the amount of pore volume of a charcoal that is filled by mercury under a given pressure and again making use of the Kelvin equation, to calculate the distribution.

A very successful application of these ideas has been made by Juhola and Wiig (5, 6) who measured the pore distributions by the second method outlined above and also determined the water isotherms on the same charcoals. They substituted the values for the pore radii obtained from the area-volume measurements in the Kelvin equation and making use of their water desorption data,

<sup>1</sup> Manuscript received October 1, 1951.

Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Also issued as DRCL Report No. 77.



calculated the angle of wetting,  $\theta$ . In earlier work with the Kelvin equation, the wetting angle was always assumed to be zero, which meant  $\cos \theta$  was equal to one. Juhola and Wiig found  $\cos \theta$  to approximate 0.5.

Recently Barrett, Joyner, and Halenda (1) have published a general method for calculating pore size distributions in porous solids from low temperature nitrogen adsorption isotherms. This method makes use of a postulate by Wheeler (9), that when desorption occurs by evaporation from a meniscus in a capillary, a physically adsorbed layer of determinate thickness remains. The radius of the pore inside this adsorbed layer is given by the Kelvin equation. Wheeler originally calculated the thickness of the adsorbed film from the BET equation (2), however this is known to give results which are too high in the region of high relative pressures. Barrett, Joyner, and Halenda used the experimental data of Shull (8) for multilayer adsorption on crystalline materials. Their estimate is probably slightly low, since the film would be expected to be a little thicker on the curved surface of a pore than on a flat surface.

In this paper, this method has been used to calculate the pore size distributions of three activated charcoals. It has been found that the pore size distributions calculated using the Kelvin equation and the desorption loops of the water isotherms for these charcoals can be brought into agreement with those calculated from the low temperature nitrogen isotherms for the same charcoals, if the angle of wetting of the water is assumed to be such that  $\cos \theta = 0.65$  in the Kelvin equation. Some general conclusions on the nature of hysteresis in nitrogen and water sorption on charcoal are drawn.

#### EXPERIMENTAL

Three different charcoals were studied: a steam activated coconut shell charcoal (Charcoal A), a sample of Charcoal A which had been further activated in a stream of hydrogen at 1000°C. (Charcoal B), and a zinc chloride activated maple sawdust charcoal (Charcoal C). The samples were all degassed by evacuating at 200°C. for at least 12 hr. before any measurements were made. Nitrogen isotherms were measured at 78°K. in a standard volumetric adsorption apparatus and the surface areas were calculated by means of the BET equation (2).

Water isotherms were determined by a gravimetric method, in which a known weight of charcoal was placed in a cell which could be detached from the remainder of the apparatus and weighed. Points on the isotherms were obtained by introducing water vapor into the apparatus with the charcoal cell attached, allowing it to equilibrate until no further pressure change was observed, and then closing off the cell, detaching, and weighing it. All equilibrations were carried out with the charcoal cell immersed in a 25°C. thermostat. Since this temperature was close to room temperature, it has been assumed that no appreciable adsorption or desorption occurred while the cell was being weighed. The pressures of water vapor over the charcoal were read on a mercury manometer with a cathetometer.

Pore volumes were computed from the difference in the densities of the charcoals when immersed in mercury and in benzene.

## RESULTS

The surface areas and the pore volumes of the three charcoals are tabulated below.

	Surface area, m. <sup>2</sup> per gm.	Pore volume, cc. per gm.
Charcoal A	1375	0.81
Charcoal B	1610	0.95
Charcoal C	1530	1.10

The low temperature nitrogen isotherms have been plotted in Figs. 1 and 2 and the water isotherms in Figs. 3 and 4. The pore distributions of the charcoals were calculated from both the nitrogen and the water isotherms, using the method of Barrett, Joyner, and Halenda (1) for the nitrogen and the Kelvin equation for the water data. In using the Kelvin equation a value of 0.65 was used for  $\cos \theta$ . The calculated pore distribution for Charcoal A is shown in Fig. 5, where the solid line gives the results from the nitrogen isotherm and the circles are values from the water isotherm. The dotted line represents the water values if  $\cos \theta$  is made equal to unity. Fig. 6 shows the corresponding curves for the other two charcoals.

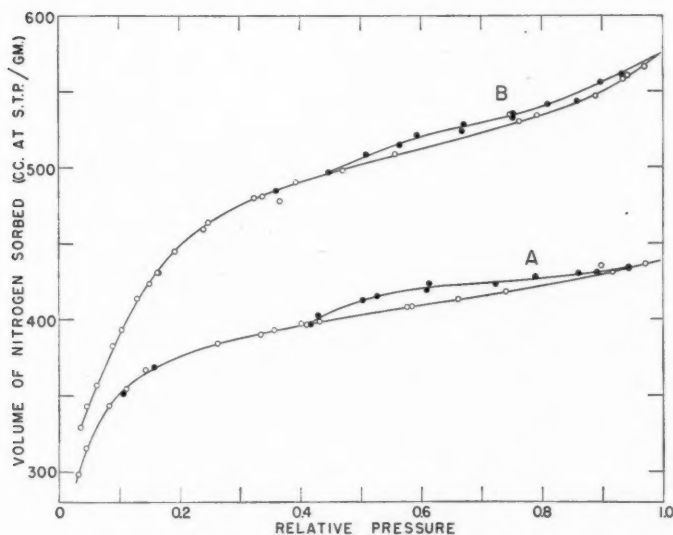


FIG. 1. Low temperature nitrogen isotherms for Charcoals A and B.  
○ Adsorption. ● Desorption.

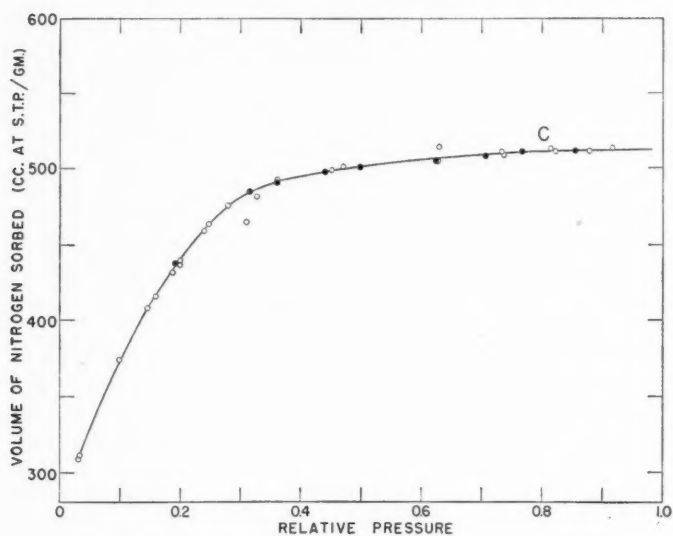


FIG. 2. Low temperature nitrogen isotherm for Charcoal C.  
○ Adsorption. ● Desorption.

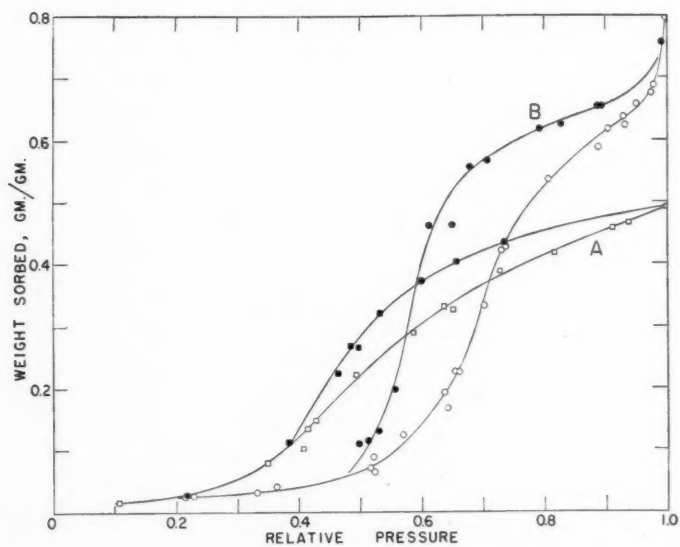


FIG. 3. Sorption isotherms at 25°C. for Charcoals A and B. Open symbols denote adsorption. Solid symbols denote desorption.

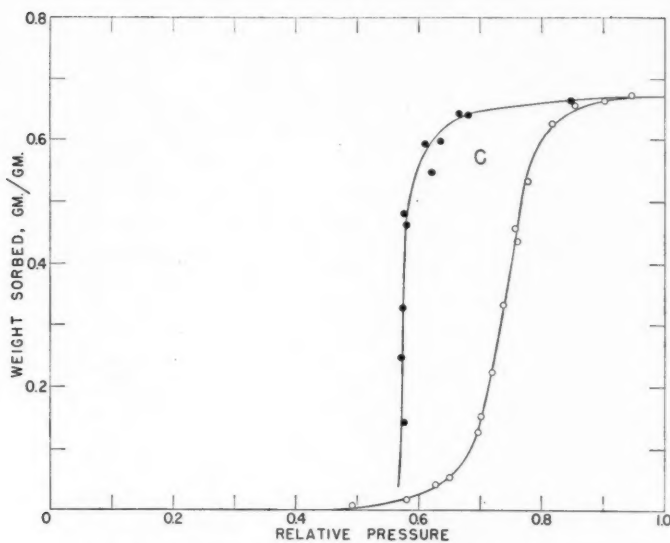


FIG. 4. Sorption isotherms at 25°C. for Charcoal C.  
 ○ Adsorption. ● Desorption.

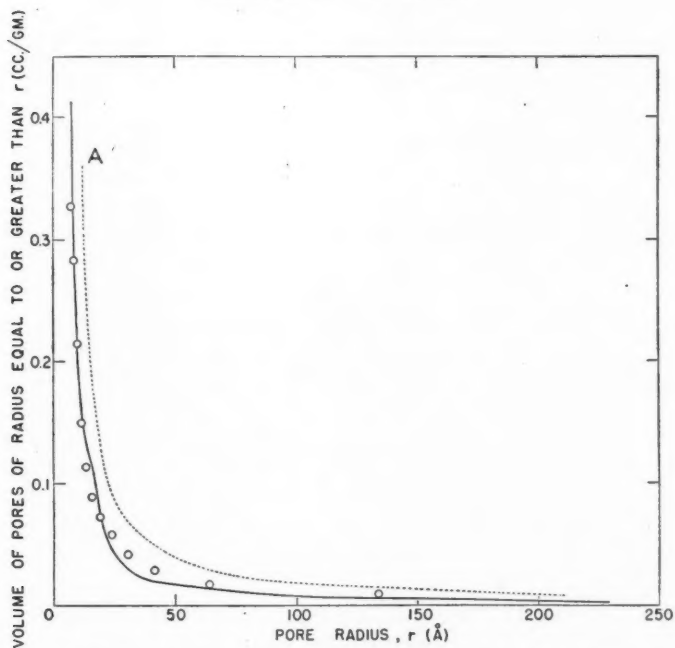


FIG. 5. Pore distribution for Charcoal A. Solid line calculated from the nitrogen isotherm. Circles calculated from the water isotherm. Dotted line from the water isotherm using a value of unity for  $\cos \theta$ .

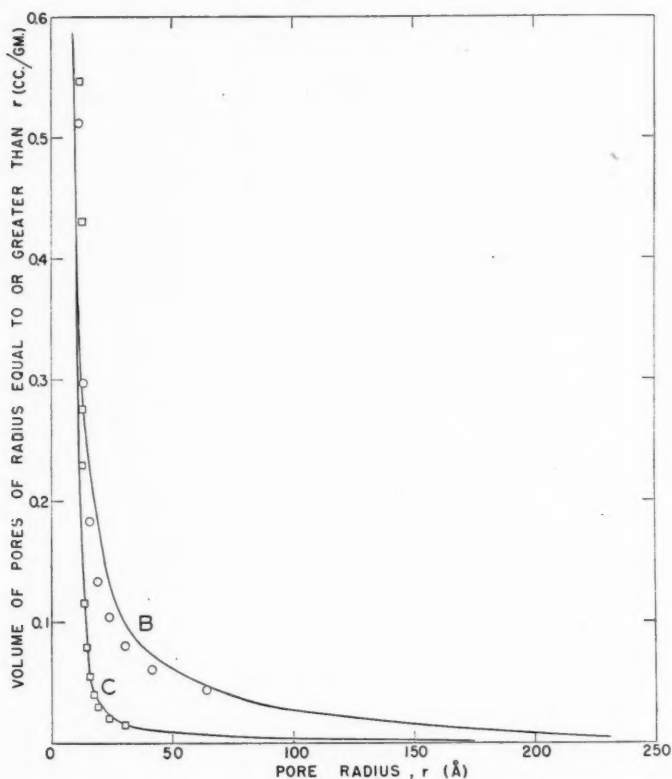


FIG. 6. Pore distributions for Charcoals *B* and *C*. Solid lines calculated from the nitrogen isotherms. Open symbols calculated from water isotherms.

#### DISCUSSION

Figs. 5 and 6 show that if  $\cos \theta$  is assigned a value of 0.65 in the Kelvin equation, the pore distributions calculated from the water isotherms are in general agreement with those obtained from the nitrogen isotherms using the Barrett, Joyner, and Halenda method. This use of  $\cos \theta = 0.65$  when calculating pore radii from isotherms of the water sorption on charcoal is slightly higher than a value obtained by Juhola and Wiig (5) for the same systems by quite a different method. A value of this order is to be expected on purely theoretical grounds, as it is generally recognized that activated charcoal surfaces are essentially hydrophobic and therefore the angle of wetting would be appreciably greater than  $0^\circ$ .

It is considered that the mechanism of water sorption by charcoal is quite different from the low temperature nitrogen adsorption. As the charcoal surface is hydrophobic, there is no physical adsorption on the surface, instead the water

molecules are attracted to active centers consisting probably of chemisorbed oxygen or similar groups. This principle of active centers has already been put forward by Pierce and Smith (7) for the sorption of water by charcoal. At these active centers the water molecules build up multilayers by a mechanism of hydrogen bonding and when these localized collections of water molecules are large enough, several coalesce and a filled pore results. It is hoped that experiments presently underway will confirm this view. In contrast to this mechanism of water sorption, nitrogen adsorption can be viewed as simple layer formation over the entire surface with capillary condensation occurring as the filling of the pores approaches completion, as has been postulated by Wheeler (9). The desorption mechanism can be considered to be essentially the same for both systems during the early stages of desorption and might be termed "capillary evaporation," although it must be recognized that some physical desorption from the residual multilayers will also occur in the case of nitrogen. This visualizes the evaporation of sorbate molecules from the menisci of filled pores. The difference in the later stages of the desorption cycle lies in the fact that in the case of the water desorption, the capillary evaporation continues until the bare adsorbent surface remains, while with nitrogen adsorbed multilayers remain and reversible physical desorption completely replaces the capillary evaporation during the latter stages of the cycle.

It may be seen from Figs. 3 and 4 that hysteresis was observed in the nitrogen isotherms of Charcoals *A* and *B*, but was absent in that of Charcoal *C*. In the first two cases the hysteresis began at a relative pressure of approximately 0.4, which corresponds to a pore radius of about 18 Å. The film thickness at this relative pressure according to the data of Shull (8) is approximately 6 Å., which has the effect of reducing the size of the meniscus from which desorption occurs to about six molecular diameters. Cohan (3) has pointed out that according to the delayed meniscus theory, hysteresis will only occur in pores greater than four molecular diameters across. These results are essentially in agreement, if it is recognized that Shull's data are for plane surfaces. The film thickness on a curved surface would be expected to be greater, which would have the effect of reducing the effective diameter for evaporation. The absence of hysteresis in Charcoal *C* can also be accounted for on this basis. As Figs. 5 and 6 show, approximately 16% of the total pore volume available to nitrogen in Charcoals *A* and *B* consists of pores having radii of 18 Å. or larger, while in Charcoal *C* this figure is only 4%. If hysteresis only occurs in these larger pores, then it is clear that small hysteresis loops should be found with Charcoals *A* and *B* and that the loop would be virtually absent with Charcoal *C*.

The experiments reported here appear to support the view that there is a difference in the mechanism of the desorption of nitrogen and water from charcoal and that the assumption of capillary evaporation with residual multilayers in the case of nitrogen and capillary evaporation alone in the case of water appears adequate to account for the difference. It has also been shown that it is possible to calculate consistent pore distribution data from the two types of isotherms.

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## INVESTIGATION OF THE FORMS OF PHOSPHORUS IN NEUTRON-BOMBARDED PHOSPHATES

### III. SUPERPHOSPHATE AND CALCIUM SULPHATE HEMIHYDRATE<sup>1</sup>

BY J. G. A. FISKELL,<sup>2</sup> W. A. DELONG, AND W. F. OLIVER

#### ABSTRACT

Carrier-precipitation and serial molybdate precipitation procedures for the identification and estimation of chemical forms of phosphorus are presented in some detail. Application of these methods to the investigation of the forms of phosphorus-32 in superphosphate and calcium sulphate after neutron bombardment is described. The results obtained indicated that about 40% of the phosphorus-32 in the superphosphate was in the orthophosphate form and that the greater part of the remainder was present as metaphosphate and phosphite. Approximately 90% of the radioactive phosphorus present in the calcium sulphate was estimated to be in the orthophosphate form. The amount of phosphorus-32 in the superphosphate originating from the calcium sulphate component was estimated to be less than 0.2%.

#### INTRODUCTION

The authors (6) have presented evidence for the presence of ortho-, hypo-, pyro-, and metaphosphate forms of phosphorus-32 in neutron-bombarded calcium phosphates. The present communication deals with the investigation of the chemical forms of phosphorus in the complex substance superphosphate, and with the estimations of the forms and the amount of phosphorus-32 arising from the neutron-bombardment of this material and of one of its major components, calcium sulphate, under closely similar conditions of neutron flux. The reagents used and the analytical procedures employed are described in some detail.

The assumptions upon which the analytical techniques employed were based are as follows:

- (a) That oxidation of nascent radioactive phosphorus atoms would be expected to result in products normally formed in the oxidation of phosphorus-31, namely, orthophosphate, hypophosphate, phosphite, and hypophosphite (12, 15, 16);
- (b) That the high energy in the system (13) might result also in the production of metaphosphate, pyrophosphate, and polyphosphate;
- (c) That exchange reactions among different chemical forms of phosphorus in the oxidized state do not occur (4, 8, 9, 17, 20, 21);
- (d) That the addition, to solutions containing such forms of phosphorus-32 in minute amounts, of relatively large quantities of corresponding chemical forms of phosphorus-31 would tend to inhibit hydrolytic and other changes in the case of the less stable forms of the radioactive materials;

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(e) That a given chemical form of phosphorus-32 could be expected to separate from solution on precipitation of a phosphorus-31 carrier of the same chemical form.

#### EXPERIMENTAL REAGENTS AND MATERIALS

The preparation and testing of substances used as carriers were as described below.

##### *Orthophosphate*

The orthophosphate phosphorus of reagent grade disodium phosphate was precipitated as ammonium phosphomolybdate under the conditions prescribed by Jones (10), the product then was dissolved and doubly precipitated as magnesium ammonium phosphate under the conditions and observing the precautions advised by Kolthoff and Sandell (11). The magnesium salt finally was washed with dilute ammonia solution followed by two washings with ethanol and one with ether, after which it was equilibrated with and stored in an atmosphere of 50% relative humidity to ensure formation of the hexahydrate (14). A similar preparation of this salt containing phosphorus-32 was made from neutron-bombarded material, all phosphorus present first being converted to the orthophosphate form as described previously (5, 6). In the case of the latter preparation, radioactivity other than that due to orthophosphate could not be detected when solutions of the salt were tested by carrier precipitations of hypophosphate, metaphosphate, pyrophosphate, or polyphosphate as described below.

##### *Pyrophosphate*

Calcium pyrophosphate was prepared by the interaction of stoichiometric amounts of tetrasodium pyrophosphate and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , both of C.P. grade, in aqueous solution at  $80^\circ\text{C}$ ., the product being washed with water and with ethanol. The calcium salt was recrystallized from water, washed with ethanol, and dried at  $100^\circ\text{C}$ . Analyses for orthophosphate and for metaphosphate by the methods of Jones (10) showed that the recrystallized product did not contain detectable amounts of these forms of phosphorus. Analysis for calcium and for phosphorus, and determination of the loss in weight on heating to  $500^\circ\text{C}$ ., indicated that the product was calcium acid pyrophosphate with less than one molecule of water of hydration. The pyrophosphate content of the salt, as determined by the method of Bell (3), indicated that all the phosphorus was present in the pyrophosphate form.

In the majority of instances the calcium salt just described was used as the pyrophosphate carrier, but, in some of the earlier work, commercial tetrasodium pyrophosphate of reagent grade was employed.

##### *"Hexametaphosphate"*

Commercial sodium "hexametaphosphate", C.P., was used as the metaphosphate carrier. Analysis of this salt for phosphorus in the "hexametaphosphate" form using the method of Jones (10) indicated that 95% was present in this state. Analysis for ortho-, pyro-, and polyphosphate by the procedures described later in this paper showed that these forms of phosphorus were not present in this salt in detectable amounts. The filtrate obtained in the separation of the

barium metaphosphate contained 5% of the phosphorus of the sample taken. According to Jones (10) this result can be ascribed to the presence of "trimetaphosphate".

#### *Polyphosphate*

A mixture of 10 gm. of monosodium and 20 gm. of disodium phosphate, both reagent grade, in a platinum crucible was dried at 105°C., transferred to a muffle furnace at about 250°C. for two hours when the temperature was raised to about 400°C. for a further eight hours, after which the mix was melted by increasing the temperature to approximately 750°C. This final temperature was maintained for 14 hr. then allowed to drop to 180°C. during an interval of about eight hours, the solidified melt then being transferred to a desiccator for transition to room temperature. This procedure is closely similar to that used by Jones (10) for the preparation of "tripolyphosphate". Analysis of the product obtained as outlined by the method of van Wazer (19) indicated, however, that the average number of phosphorus atoms per molecule was somewhat greater than three. Further examination of the product by the methods employed in the present investigation and described below indicated that 98% of the phosphorus was present as "polyphosphate", 2% as pyrophosphate, and that orthophosphate and "hexametaphosphate" were not present in more than trace amounts. This product was used as the "polyphosphate" carrier.

#### *Hypophosphate*

Sodium dihydrogen hypophosphate was prepared essentially as in the method of Leininger and Chulski (12) except that the initial step consisted of the reaction of red phosphorus with an aqueous solution of technical sodium chlorite in a large Erlenmeyer flask. The product was thrice recrystallized from aqueous solution. The fact that essentially all of the phosphorus of the recrystallized substance was precipitable as the silver salt at pH 1.5 in the presence of either formic acid or orthophosphoric acid indicated that it was practically 100% in the hypophosphate form.

A calcium hypophosphate preparation was obtained by adding calcium nitrate solution to a solution of the sodium salt until no further precipitation occurred. The gelatinous product was filtered and washed twice with water and twice with dilute aqueous ethanol (1 + 1) and dried at 100°C. All of the phosphorus of this calcium salt also was precipitable with silver nitrate at pH 1.5 in the presence of orthophosphoric acid.

Both the sodium and the calcium salt were used as hypophosphate carriers.

#### *Ammonium Phosphite*

Reagent grade phosphorus trichloride and distilled water were allowed to react under reduced pressure in a suction flask cooled by an ice-water mixture, the trichloride being added dropwise from a separatory funnel. The reaction mixture was taken to small volume on the steam bath and the ammonium salt formed by addition of ammonium hydroxide in slight excess of a one-to-one ratio of ammonia to phosphorus. The salt was precipitated by addition of ethanol and filtered, the product being washed several times with ethanol to

remove ammonium chloride and any ammonium hypophosphite formed. The salt was redissolved in water, reprecipitated with ethanol, and dried at 100°C. Analysis for ammonia, for total phosphorus, and for phosphite phosphorus, the latter by the method of Wolf and Jung (22), indicated that the product was ammonium phosphite and that orthophosphate and hypophosphite were absent. This product was used as a carrier for phosphite.

#### *Hypophosphite*

Potassium hypophosphite was allowed to react with  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , C.P., in warm 50% ethanol solution. The precipitate was filtered and washed several times with ethanol. Recrystallization from 50% ethanol was followed by drying at 100°C. Analysis of this product and of the original potassium salt, using the methods of this investigation, indicated the absence of detectable amounts of phosphorus in the orthophosphite, or the ortho-, pyro-, meta-, or hypophosphate forms. Both the potassium and the calcium salt were used as carriers for hypophosphite.

Reagent solutions used in the precipitation of phosphates, with the volumes employed per 0.1 gm. of phosphorus pentoxide were as follows:

Ammonium molybdate; 60 ml. This reagent was essentially similar to that used by Jones (10) for the separation of orthophosphate except that it was prepared from ammonium molybdate instead of from molybdic acid plus ammonium hydroxide, and that the molybdate concentration was increased from about 0.46 *M* to about 0.59 *M*.

Magnesia mixture; 30 ml. This was the concentrated magnesia mixture of Kolthoff and Sandell (11).

Barium chloride; 70 ml.; the reagent of Jones (10).

Zinc sulphate; 30 ml.; the reagent of Bell (3).

Silver nitrate; used in slight excess; 1.0 *M*.

#### *Materials*

The superphosphate sample was taken from screenings (passing the 10- and refusing the 40- mesh per inch sieves) from a bag of the commercial product made by the Oberfos process. The sample was dried at 105°C. overnight and kept in a closed container before and after the neutron bombardment. The phosphorus in the superphosphate sample was 50% water-soluble and totally soluble in neutral ammonium citrate by the procedures generally recommended (2). Comparison of the X-ray diffraction pattern of the powdered sample with that recorded (1) indicated that the calcium sulphate was present as the hemihydrate.

Gypsum, C.P. grade, was heated overnight in the drying oven at 105°C. This product also gave the diffraction pattern of the calcium sulphate hemihydrate.

The phosphorus content of the gypsum was less than five parts per million. That of the superphosphate was 10% by weight and 90% was precipitated by the molybdate reagent at room temperature (23°C.) in 15 min., as in the APM I procedure given below; the remaining phosphorus was precipitable on heating this filtrate at 70°C. for one hour, as in the APM II procedure.

## EXPERIMENTAL RESULTS AND CONCLUSIONS

Preliminary experiments showed that when neutron-bombarded superphosphate was dissolved and the phosphorus precipitated under the conditions given by Kolthoff and Sandell (11), less than 5% of the radioactivity, as measured by the dipping counter technique of Solomon *et al.* (18), remained in the filtrate. Further investigation revealed that, in solutions containing calcium ions in amounts comparable to those in the superphosphate solution, treatment with magnesia mixture under the conditions noted above caused precipitation not only of phosphorus in the orthophosphate form, but also of the pyro-, meta-, hypo-, and polyphosphate forms, and of orthophosphite as well. Phosphorus in the hypophosphite form was not precipitated under these conditions. Also, in absence of calcium, only trace amounts of polyphosphate and orthophosphite were precipitated by the magnesia mixture under these conditions.

Two analytical schemes were developed for the solution of the problem of the chemical forms of phosphorus-32 in neutron-bombarded calcium phosphates, one based on the individual precipitation of carrier substances, the other involving serial precipitation of the phosphorus of carrier substances as ammonium phosphomolybdate. These procedures provide, at certain points, a degree of mutual support. A combination of the two has been employed both in the previously reported work (6) and in the present investigation.

In the carrier-precipitation technique, as previously reported (6), the detection and estimation of a particular chemical form of phosphorus involves the precipitation of a carrier substance of the same chemical form in presence of carriers for all the other chemical forms suspected of being present. The methods of chemical separation employed in this connection have been as follows:

1. The procedures of Jones (10) for the separation of (a), orthophosphate as the molybdophosphate complex and (b), metaphosphate as the barium salt after removal of calcium from the carrier-containing solution.
2. The method of Bell (3) for the separation of hypophosphate plus pyrophosphate.
3. The procedure of Wolf and Jung (22) for the separation of hypophosphate alone, and a modification of this method, using formic acid instead of orthophosphoric acid to adjust to pH 1.5 prior to precipitation with silver, for the separation of hypophosphate plus metaphosphate plus polyphosphate.

The colorimetric method of Gerritz (7) was used for the determination of the total phosphorus content of solids and of solutions.

The chemical forms upon which counting was done, and the methods and precautions used in the estimation of phosphorus-32 activity, likewise the technique employed to ensure conversion of all chemical forms of phosphorus-32 (except phosphine) present in calcium-containing neutron-bombarded materials to the orthophosphate form, have been reported previously (6).

The procedure followed in the serial molybdate precipitation of the chemical forms of phosphorus-32 in neutron-bombarded samples of superphosphate and of calcium sulphate is outlined below.

A 0.100 gm. sample and 0.05 gm. each of the carriers calcium pyrophosphate, sodium "hexametaphosphate", sodium "polyphosphate", and calcium hypophosphate—also magnesium ammonium phosphate in the case of calcium sulphate samples—were placed in a dry Erlenmeyer flask, followed by 25 ml. distilled water, 5 gm. ammonium nitrate, and 60 ml. ammonium molybdate reagent. The mixture was allowed to stand for 15 min. at room temperature with frequent agitation by swirling of the flask. The ammonium phosphomolybdate precipitate obtainable under these conditions was designated APM I. The APM I was filtered, washed, converted to magnesium ammonium phosphate (as described under Reagents) and the activity determined. With the exception of a trace amount of metaphosphate-phosphorus none of the carrier substances mentioned contributed to the APM I precipitate. Throughout these investigations it has been considered that the radioactivity of the APM I precipitate provides a suitable measure of the amount of phosphorus-32 present in the orthophosphate form.

On heating the filtrate from the APM I for an hour at 75°C. the phosphorus of the meta-, pyro-, and polyphosphate carriers along with phosphorus-32 considered to be present in these forms was precipitated as ammonium phosphomolybdate. This precipitate was designated APM II. The APM II was dissolved in ammonia solution and reprecipitated as phosphomolybdate. The radioactivity of the APM II was measured in the usual manner after conversion to the magnesium salt.

To the combined filtrates from the double precipitation of APM II 30 ml. of ammonium molybdate solution were added, along with 10 ml. saturated bromine water and 0.05 gm. each of ammonium orthophosphite and potassium hypophosphite carriers. The mixture then was heated at 75°C. for two hours. The precipitate obtained was designated APM III. Radioactivity of APM III was measured in the usual manner, and was considered to represent the fraction of the phosphorus-32 present in the phosphite form.

The fate of carrier-phosphorus submitted to this scheme of analysis is summarized in Table I.

TABLE I  
OCCURRENCE OF PRECIPITATION OF CARRIER-PHOSPHORUS IN SERIAL MOLYBDATE ANALYSIS  
OF SOLUTIONS CONTAINING CALCIUM

Carrier	APM I	APM II	APM III
Magnesium ammonium phosphate	+	—	—
Calcium pyrophosphate	—	+	Trace
Sodium "hexametaphosphate"	Trace	+	Trace
Sodium "polyphosphate"	—	+	Trace
Ammonium orthophosphite	—	Trace	+
Potassium hypophosphite	—	—	+
Calcium hypophosphate	—	—	Trace

The behavior of the various carriers employed in carrier-precipitation analysis is shown in Table II. The symbols in parentheses indicate the behavior of the



TABLE II  
BEHAVIOR OF CARRIER SUBSTANCES IN SOLUTIONS CONTAINING CALCIUM UNDER VARIOUS  
CONDITIONS OF PRECIPITATION

Carrier	Precipitating reagents			
	AgNO <sub>3</sub>	AgNO <sub>3</sub>	BaCl <sub>2</sub>	ZnSO <sub>4</sub>
	Conditions			
	pH 1.5-2.0 by HCOOH	pH 1.5-2.0 by H <sub>3</sub> PO <sub>4</sub>	pH 4.1	pH 3.8
Magnesium ammonium phosphate	—	—	—	—
Sodium or calcium hypophosphate	+	+	— (Trace)	+
Calcium pyrophosphate	—	—	+	+
Sodium "hexametaphosphate"	+	—	+	Trace
Sodium "polyphosphate"	+	—	—	Trace
Ammonium orthophosphate	—	—	—	—
Potassium hypophosphite	Silver pptd.	Silver pptd.	—	—

chemical forms opposite which they occur in solutions which do not contain calcium.

In the application of the carrier-precipitation technique to solutions containing phosphorus-32 estimates of radioactivity were made directly on the precipitates of the carriers employing the customary precautions essential to accuracy.

Inspection of Table II shows that the following forms of phosphorus may be separated from mixtures of these carriers without significant interference, namely:

(a) Metaphosphate by barium precipitation, provided that calcium-ion first is removed;

(b) Hypophosphate by silver precipitation in presence of orthophosphoric acid, provided hypophosphite is absent;

(c) Hypophosphate plus pyrophosphate by zinc precipitation, which permits estimation of pyrophosphate by difference;

(d) Hypophosphate plus metaphosphate plus polyphosphate by silver precipitation in presence of formic acid, which permits of estimation of polyphosphate by difference.

Reference to Table I indicates that the pyrophosphate, metaphosphate, and polyphosphate forms may be separated in APM II without significant interference. Since the first two of these forms can be estimated by carrier-precipitation, a second estimate of polyphosphate may be obtained by difference. The serial molybdate technique also provides for the estimation of the phosphite form.

The distribution of the radioactivity due to phosphorus-32 in neutron-bombarded superphosphate among the various chemical forms of phosphorus separated in fractionation with carrier substances is presented in Table III.

Consideration of the data of Table III leads to the conclusion that the major chemical forms of phosphorus-32 present in the sample of neutron-bombarded



TABLE III  
DISTRIBUTION OF PHOSPHORUS-32 RADIOACTIVITY IN NEUTRON-BOMBARDED SUPERPHOSPHATE

Conditions of separation	Chemical forms separated	Counts per minute* for individual determinations	Estimated % of total phosphorus-32
APM I	Orthophosphate	2641, 2742, 2890, 2687	39
APM II	Metaphosphate + pyrophosphate + "polyphosphate"	2769, 2683, 2334, 2548	37
APM III	Phosphite	1206, 1094, 1220, 1164	17
	Unaccounted		7
Ba salt, pH 4.1, Ca-free	Metaphosphate	1875, 1828, 1904	27
Zn salt, pH 3.8	Hypophosphate + pyrophosphate	658, 740, 462	10
Ag salt, pH 1.5-2.0, H <sub>3</sub> PO <sub>4</sub>	Hypophosphate	452, 508, 423, 462	7
	Pyrophosphate by difference, 10-7		3
Ag salt, pH 1.5-2.0, HCOOH	Metaphosphate + hypophosphate + "polyphosphate"	3198, 3240, 3145, 3220	46
	"Polyphosphate" by difference, 46-(27 + 7)		12
	"Polyphosphate" by difference, 37 (APM II)-(27+3)		7

\* Total counts always greater than 10,000; minimum counting time 10 min.

superphosphate under examination were orthophosphate and metaphosphate. These forms account for about 66% of the total phosphorus-32 activity. The next most abundant form appears to be phosphite. It may be noted that the sum of the estimates obtained for the percentages of the activity occurring in the chemical forms estimated directly or by difference, namely, ortho-, meta-, hypo-, pyro-, and polyphosphates and phosphite, amounts to 100 or 105% of the total phosphorus-32 activity determined directly on the superphosphate with suitable screening out of calcium activity, that is, 6930 counts per minute. The general conclusion drawn is that neutron-bombardment of this material, as well as of the simpler calcium phosphate systems previously reported upon

TABLE IV  
DISTRIBUTION OF PHOSPHORUS-32 RADIOACTIVITY IN NEUTRON-BOMBARDED CALCIUM SULPHATE HEMIHYDRATE, (CaSO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O

Conditions of separation	Chemical forms separated	Counts per minute for individual determinations	Estimated % of total phosphorus-32
APM I	Orthophosphate	977, 925, 982, 969	90
APM II	Metaphosphate + pyrophosphate + polyphosphate	104, 100, 110, 118	10
Ba salt, pH 4.1, Ca-free	Metaphosphate	98, 112, 89, 113	10

(6), results in the production of a considerable variety of chemical forms of phosphorus-32.

The data obtained in the analysis of the neutron-bombarded sample of calcium sulphate which was investigated are reported in Table IV.

In this analysis only traces of radioactivity were found in the APM III precipitate and in the silver salt separated at pH 1.5-2.0 in presence of orthophosphoric acid. The conclusion drawn from these facts and from the data of Table IV is that the phosphorus-32 of the sample was nearly all in the orthophosphate form, the remainder being accounted for as metaphosphate.

From the total phosphorus-32 radioactivity of this sample, which had been neutron-bombarded under very closely similar conditions to those employed for the sample of superphosphate, it was calculated that the contribution of the calcium sulphate in the latter to its phosphorus-32 activity was less than 0.2%.

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## THE MERCURY PHOTSENSITIZED REACTIONS OF NITRIC OXIDE<sup>1</sup>

By J. D. MCGILVERY AND C. A. WINKLER

### ABSTRACT

The photochemical decomposition of nitric oxide has been studied over a pressure range 60 to 500 mm., using a low pressure mercury arc source and a circulating system. Stoichiometrically, the reaction was found to be represented by  $6\text{NO} \rightarrow \text{N}_2 + 2\text{N}_2\text{O}_3$ . Addition of nitrogen decreased the rate, as did also a decrease in the mercury vapor pressure. Using appropriate light filters at  $1.7 \times 10^{-3}$  mm. mercury pressure the decomposition was shown to be photosensitized by Hg (6<sup>1</sup>P<sub>1</sub>) atoms. The primary process is probably dissociation of nitric oxide into nitrogen and oxygen atoms.

### INTRODUCTION

The photochemical decomposition of nitric oxide has been the subject of several previous investigations of which the most recent and most detailed are those of Noyes (11) and of Flory and Johnston (2).

Noyes employed a medium pressure water cooled mercury arc as a light source and investigated the reaction over a pressure range from 0.002 to 24 mm. Under these experimental conditions he found the decomposition to be mercury photosensitized by the 2537 Å resonance line. The energy associated with this line is insufficient to dissociate the nitric oxide molecule directly and Noyes postulated the formation, by collisions of the second kind, of a nitric oxide molecule in the 26th or 27th vibrational level of the normal electronic state. It also followed from his results that the mean life of this activated molecule must be comparatively long.

Flory and Johnston studied the reaction over a pressure range from 0.02 to 7 mm. using a mercury arc lamp in which the 2537 Å line was almost completely reversed and found at least 98% of the decomposition to be due to direct photolysis. By the use of appropriate filters and by comparison of the absorption spectrum of nitric oxide with the emission spectrum of mercury they concluded that the 1832 Å mercury line was responsible for the bulk of the decomposition at low pressure and suggested that the 1849 Å line might play a dominant role at higher pressures.

The present paper is the result of an attempt to obtain further information about the photochemical decomposition of nitric oxide.

### EXPERIMENTAL

A combination lamp and reaction vessel (16)\* surrounded by an electric furnace was used in this investigation. The arc was of the low pressure neon-mercury type enclosed in a quartz tube and surrounded by a quartz jacket over four-fifths of its length, into which appropriate filter solutions could be intro-

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duced. The reactant was circulated through a pyrex envelope enclosing the inner quartz jacket and arc. The quantum output of 2537 Å radiation, determined with monochloroacetic acid (14), was  $1.7 \times 10^{-6}$  einsteins per second with the inner jacket evacuated.

The system was evacuated through a U-tube which could also serve as a manometer. Gas was circulated by a rocking mercury pump at a flow rate of about 800 cc. per minute. The gases were saturated with mercury vapor at 25°C. by passing them over a pool of mercury at 60°C., and then through a trap filled with iron pellets at 25°C. Samples of gas for analysis were taken with a Toepler pump and analyzed with an apparatus of the Bone-Wheeler type (1).

Nitrogen dioxide, a product of the reaction was immediately absorbed (7) by reagent grade potassium hydroxide pellets in a trap at the reaction vessel exit, according to the reaction (in the presence of excess nitric oxide)



The potassium nitrite formed was estimated volumetrically (13). Preliminary studies with known nitrogen dioxide - nitric oxide mixtures showed the nitrogen dioxide analysis to be quantitative over the range of concentrations encountered in the study.

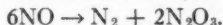
Nitric oxide was determined by absorption in acidified ferrous sulphate solution, and oxygen by absorption in alkaline pyrogallol solution. Unabsorbed gas was assumed to be nitrogen.

Nitric oxide (98.5% pure, from Matheson Company, N.J.) was condensed in a liquid nitrogen trap, from which it was sublimed into the system. It was freed from nitrogen by repeatedly subliming and condensing it and pumping off the uncondensable gas.

## RESULTS

### *Stoichiometry of the Reaction*

To ensure proper interpretation of data obtained by pressure measurements the stoichiometry of the reaction was examined at various nitric oxide pressures. It was found that if the partial pressure of nitric oxide in the system at the conclusion of an experiment exceeded about 50 mm., a good material balance was obtained in accordance with the over-all reaction



At lower final partial pressures of nitric oxide, however, there was an apparent nitrogen excess and oxygen deficit in the material balance, and the magnitude of these deviations increased rapidly with decreased nitric oxide pressure. It was further noted that at the lower pressures, compression of the gases in the Toepler pump caused the brown fumes of nitrogen dioxide to appear and a film to form on the mercury surface, while at high nitric oxide pressures, compression of the gases had no apparent effect. Also, at low nitric oxide pressures, small amounts of free oxygen were found in the system.

These observations are readily explained if oxygen is one of the products of decomposition. Reaction of oxygen with nitric oxide to form the dioxide, a third order reaction, might be expected to be relatively rapid at high nitric oxide

pressures, the nitrogen dioxide formed being removed by the potassium hydroxide so that no oxygen remains. At low nitric oxide pressures, however, where formation of the dioxide would be slower, oxygen might accumulate in the reaction mixture and form the dioxide only under compression in the Toepler pump during the sampling procedure. Reaction of nitrogen dioxide with mercury in the pump would account for the film on the mercury surface, and would increase the ratio of nitrogen to oxygen in the sample taken for analysis, corresponding to the apparent nitrogen excess and oxygen deficiency observed.

With the stoichiometry of the over-all reaction established for partial pressures of nitric oxide in excess of about 50 mm. of Hg, it was possible under such conditions to calculate the partial pressure of nitric oxide present at any time from the initial pressure of nitric oxide and the observed pressure at time  $t$ .

The equation relating these pressures is

$$P_{\text{NO}} = 1/5 (6P - P_0),$$

where  $P_{\text{NO}}$  is the partial pressure of nitric oxide at time  $t$ ,

$P$  is the observed pressure at time  $t$ ,

$P_0$  is the initial pressure of nitric oxide.

For this equation to apply directly, the whole system must be at a constant temperature. Experimentally, however, the reaction vessel was always at a temperature some 50° or more higher than that of the remainder of the system, which was at room temperature. The pressure corresponding to the entire system at the temperature of the reaction vessel was therefore calculated and used in the above equation.

The effect of nitrogen accumulation in the system on the rate was obtained by making several experiments in which a constant initial amount of nitric oxide was diluted with various amounts of nitrogen and the amount of nitrogen trioxide formed after 45 min. determined. The nitrite analysis was used because

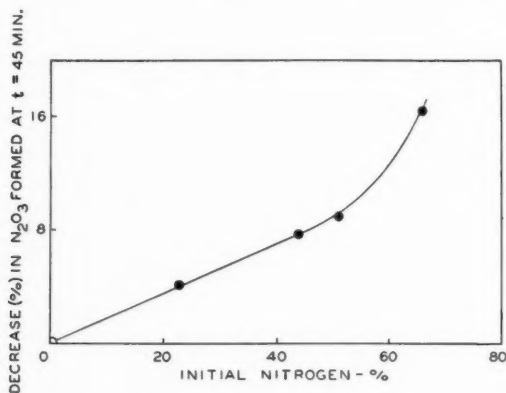


FIG. 1. Effect of the addition of nitrogen on the amount of decomposition after 45 min. when the initial partial pressure of nitric oxide is held constant.

it was more sensitive than pressure measurements and the effect was expected to be rather small.

The results obtained are shown graphically in Fig. 1. Even at the lowest pressures used in the rate experiments with pure nitric oxide the amount of nitrogen accumulated in the system rarely exceeded 40%. The maximum retardation of the rate therefore was of the order of 7% and the error could be neglected.

The effect of temperature on the reaction appeared to be complicated by self-reversal of the mercury line causing the decomposition. Thus it was found that when the mercury droplet in the arc tube was located in the emitting portion of the tube within the confines of the furnace, an increase of temperature from 68°C. to 115°C. reduced the reaction rate by about 70%. This implied either a chemical reaction with a large negative temperature coefficient or a decrease in the output of effective radiation by some physical process such as self-reversal. Since it was found that with the mercury droplet located in the electrode chambers externally to the furnace the reaction rate at 78°C. was greater than the rate at 68°C. with the droplet in the arc tube, it seemed reasonable to assume that self-reversal of the resonance line was the cause of the decreased rate.

Experiments were made over a range of initial nitric oxide pressure from 60 to 315 mm. of Hg, the mercury vapor pressure in the system being about  $1.7 \times 10^{-3}$  mm. In Table I are shown the results obtained:

TABLE I  
EFFECT OF NITRIC OXIDE PRESSURE ON THE RATE OF DECOMPOSITION WITH A VAPOR PRESSURE  
OF MERCURY IN THE SYSTEM OF  $1.7 \times 10^{-3}$  mm.  
LAMP TEMPERATURE = 56°C.

Time, min.	Nitric oxide pressure, mm.				
	62.4	83.8	110.8	231.0	312.6
0	62.4	83.8	110.8	231.0	312.6
5	60.2	80.2	108.2	228.2	310.1
10	57.2	78.4	104.8	226.8	306.4
15	55.3	75.4	102.0	225.0	
20	52.3	72.8	99.1	220.7	300.4
25	50.3	69.8	96.7		
30	48.0		93.4	216.0	293.5
35	45.6	65.5	91.0		
40	42.7	62.9	88.6	209.9	286.7
45	40.9	60.0	85.8		
50	39.2	57.8	82.8	202.8	280.1
55			80.5		
60			77.9		273.4

In another series of experiments the effects of nitric oxide pressure on the rate of decomposition was determined at a very low mercury vapor concentration.

The mercury was removed from the saturator, and traps in the circulatory system were immersed in dry ice-methanol baths maintained at -78°C. These precautions decreased the mercury vapor pressure in the reaction vessel to about  $1 \times 10^{-9}$  mm.

In Table II are shown the results obtained under these conditions:

TABLE II

EFFECT OF NITRIC OXIDE PRESSURE ON THE RATE OF DECOMPOSITION WITH A VAPOR PRESSURE OF MERCURY IN THE SYSTEM OF  $1 \times 10^{-9}$  mm.LAMP TEMPERATURE =  $50^{\circ}\text{C}$ .

Time, min.	Nitric oxide pressure, mm.				
0	111.5	214.2	270.0	365.1	484.2
5	110.1	211.6	268.8	363.7	483.3
10	109.0	210.0	268.0	361.9	481.5
20	108.3	206.6	265.2	358.6	477.0
30	105.9	203.0	261.0	354.6	472.4
40	103.9	200.4	258.2	350.7	467.4
50	101.9	197.1	254.5	346.6	463.2
60	100.3	193.7	251.0	342.2	458.8
70	98.7	191.1	247.8	338.6	455.9
80		187.8		334.5	449.3

By plotting nitric oxide pressure as a function of time for the data noted in Tables I and II and drawing tangents to the curves so obtained, the relations between reaction rate and nitric oxide pressure were obtained. These are shown in Fig. 2. It will be noted that reduction of the mercury vapor concentration markedly decreased the rate of reaction and also altered the relation between reaction rate and nitric oxide pressure.

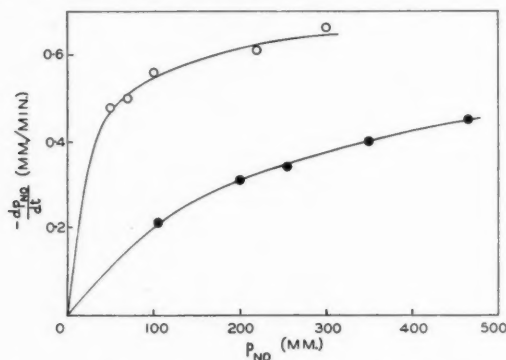


FIG. 2. The effect of mercury vapor concentration on the rate of decomposition.

○ Mercury vapor pressure  $1.7 \times 10^{-9}$  mm.● Mercury vapor pressure  $1 \times 10^{-9}$  mm.

Since there are only two resonance lines in the mercury spectrum any photo-sensitized decomposition must be caused by either  $2537 \text{ \AA}$  or  $1849 \text{ \AA}$  radiation.

From absorption data reported by Ley and Arends (8) it was estimated that with the inner jacket of the light source filled with  $0.0013 M$  solution of  $\text{NH}_4\text{Cl}$  more than 95% of the  $2537 \text{ \AA}$  and less than 0.1% of any  $1849 \text{ \AA}$  radiation would be transmitted. To verify the transmission of  $2537 \text{ \AA}$  radiation, monochloroacetic acid was used to calibrate the lamp output with and without the inner jacket filled with filter solution. The output was found to be the same within the limits of experimental error. However, a drastic reduction in the rate of



decomposition of nitric oxide was observed when this filter solution was in the inner jacket. Thus, at an initial nitric oxide pressure of about 150 mm. and with the system saturated with mercury vapor at 25°C. the rate was only 0.13 mm. per min. as compared with a rate of about 0.58 mm. per min. for the same nitric oxide pressure with the inner jacket evacuated.

Since about 20% of the radiation from the light source was unfiltered because of lamp design, an experiment was made using a filter solution capable of removing both 1849 Å and 2537 Å radiation. With a filter solution containing about 2% ammonium chloride and 10% monochloroacetic acid, the rate of decomposition at about 150 mm. nitric oxide pressure was found to be 0.13 mm. per min., which is exactly the same as the rate observed using a filter solution capable of removing only 1849 Å radiation. It was, therefore, concluded that under the experimental conditions employed only the 1849 Å resonance line was capable of producing a mercury photosensitized decomposition of nitric oxide.

#### DISCUSSION

The experimental results obtained with 0.0013 *M* ammonium chloride filter solution in the inner jacket of the light source limit the active region of the spectrum for the decomposition (either by direct photolysis or by mercury photosensitization) of nitric oxide to wave lengths shorter than about 2100 Å. It must therefore be concluded that, if the reaction is photosensitized, the 1849 Å resonance line is responsible. Even if the reaction is not photosensitized it is possible that the active line is at 1849 Å, since this is the only emission line in this region of the mercury spectrum sufficiently intense to cause the amount of reaction observed.

From the profound decrease in rate of reaction observed when the mercury atom concentration was decreased, it may be concluded that, when the reaction system was saturated with mercury vapor at 25°C., the decomposition was essentially a photosensitized process involving mercury atoms in the  $6^1P_1$  state. This conclusion is further supported by the available absorption data for the 1849 Å line. Thus Garrett (3) found the absorption coefficient of mercury to be  $6.2 \times 10^{-11} \text{N}^*$  and Flory and Johnston (2) found that of nitric oxide to be  $4 \times 10^{-3} \text{mm.}^{-1}$ \*\* Therefore at a mercury vapor pressure of  $1.7 \times 10^{-3} \text{mm.}$  almost 98% of the radiation will be absorbed by the mercury within 0.01 mm. of the arc tube. In the same distance nitric oxide at 300 mm. pressure would absorb only about 0.01% of the incident radiation.

The nature of the processes giving rise to the observed relation between nitric oxide pressure and reaction rate, with a mercury vapor pressure of  $1.7 \times 10^{-3} \text{mm.}$ , is not at all clear. It would appear that at low nitric oxide pressures (< 50 mm.) some energy dissipating process plays an important part. Since the very large absorption coefficient of mercury for the 1849 Å line would make imprisonment of this radiation a serious matter indeed, any attempt to

\*N is in atoms per cc., the light path is in cm.

\*\*The light path of the reaction vessel was 1 cm. and this is included in the absorption coefficient.

explain the results by a Stern-Vollmer type mechanism would require that the apparent mean lifetime of the  $\text{Hg}(6^1P_1)$  be greater by a factor of at least  $10^3-10^4$  than the true natural life of these atoms. Actually, assuming this type of mechanism, an effective mean life of the order of  $10^{-9}$  sec. was found, which is in good agreement with accepted values (10). Hence, it is evident that some other process capable of reducing the quantum efficiency must be postulated.

Although deactivation by wall collision of  $\text{Hg}(6^3P_1)$  atoms would not be significant at the nitric oxide pressures employed, it might become important with  $\text{Hg}(6^1P_1)$  atoms. As noted earlier almost complete absorption of the emitted 1849 Å radiation occurs within a very short distance of the arc tube, with approximately 50% of this radiation absorbed in a path of  $2 \times 10^{-2}$  mm. The mean free path of a mercury atom in 30 mm. of nitric oxide at 56°C. is of the same order of magnitude. It follows that a significant proportion of the  $\text{Hg}(6^1P_1)$  atoms should be deactivated by wall collision; this proportion should vary inversely as the nitric oxide pressure in the absence of collisions of the second kind. Perhaps a combination of wall deactivation and a Stern-Vollmer type mechanism is a sufficient explanation for the rate-pressure relation obtained when the vapor pressure of mercury was  $1.7 \times 10^{-3}$  mm.

When the mercury vapor pressure was reduced to  $1 \times 10^{-9}$  mm., the relation found between reaction rate and nitric oxide pressure was of the type usually associated with a direct photolysis mechanism. Under these conditions only about 0.2% of the initial 1849 Å radiation would be absorbed by mercury atoms whereas roughly 70% absorption would be expected by nitric oxide at 300 mm. If it is assumed that the rate controlling factor in the direct photolysis is the rate of light absorption, then the rate equation will be

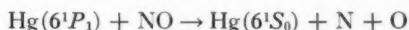
$$-\frac{dp}{dt} = \phi I_0 (1 - e^{-ap})$$

where  $a$  is the absorption coefficient of nitric oxide for 1849 Å radiation and  $\phi$  is the over-all quantum yield. Therefore a plot of  $-\frac{dp}{dt}$  vs.  $e^{-ap}$  should yield a straight line with slope  $-\phi I_0$  and intercept  $\phi I_0$ . This is found to be the case when the mercury vapor pressure is  $1 \times 10^{-9}$  mm. and the value found for  $\phi I_0$  is 0.53 mm. per min. Macdonald (9) determined the quantum yield for the decomposition of nitric oxide by radiation of wave length about 1900 Å. Applying Macdonald's data to the present investigation,  $\phi$  is found to be 2.18 for the over-all reaction. Consequently the intensity,  $I_0$ , of 1849 Å radiation is 0.24 mm. per min. or  $2.4 \times 10^{-7}$  einsteins per sec. Apparently the 1849 Å line constitutes approximately 12% of the mercury resonance radiation emitted by the lamp if the foregoing assumptions are valid.

#### *The Primary Process*

The energy associated with the wave length 1849 Å is 6.67 ev. Since a mercury atom in the  $6^1P_1$  state can be quenched only to the ground  $6^1S_0$  state, it follows that the energy transferred in every collision of the second kind will be 6.67 ev. The true heat of dissociation of nitric oxide is a matter of some debate, the pro-

posed values being 5.29 ev. and 6.49 ev. (4, 5). Whichever is correct, the reaction



is energetically possible, and offers the simplest explanation for the primary process.

It is suggested that the reduction in reaction rate noted in the presence of added nitrogen is due to the deactivation of  $6^1P_1$  mercury atoms by nitrogen. It is noteworthy that the 3rd vibrational level of the first excited electronic state of nitrogen lies at about 6.68 ev. (6) and therefore the effective quenching cross section of nitrogen might be expected to be appreciable.

#### *Secondary Atomic Processes*

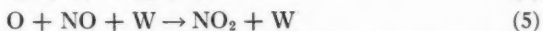
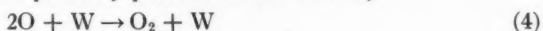
For the removal of nitrogen atoms, three secondary reactions appear to merit serious consideration (other stoichiometrically possible reactions have been discussed by Flory and Johnston (2)). These are:



It seems difficult to understand how Reactions (1) and (2) could compete with Reaction (3) which appears to occur quite readily (15, 17) and should be capable of removing most of the nitrogen atoms from the system. However the experimental evidence appears to favor Reaction (1).

If the removal of nitrogen atoms is solely by (1) or (3) the over-all quantum yield  $\phi$  will be 3 or 6 respectively. In the discussion of the mercury photosensitized reaction it was suggested that the energy dissipating processes were deactivation of excited mercury atoms at the walls and escape of fluorescent radiation. At high nitric oxide pressures these processes will become negligible and the reaction rate becomes independent of pressure and equal to  $\phi I_0$ . Therefore, assuming Reaction (1) for the removal of nitrogen atoms the limiting reaction rate will be about 0.69 mm. per min. and assuming Reaction (3) about 1.38 mm. per min. Examination of Fig. 2 indicates a leveling off at about 0.7 mm. per min. in accord with Reaction (1). However it should be pointed out that a suitable combination of (2) and (3) could reduce  $\phi$  to 3 and give the same result. Flory and Johnston (2) also concluded that Reactions (1) and (2) were adequate to account for removal of nitrogen atoms in the direct photolysis.

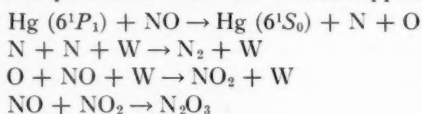
Removal of oxygen atoms probably proceeds in the main by



Reaction (4) requires a three body collision and the same is probably true for Reaction (5) also, (12). It seems likely that the reaction with nitric oxide should be highly favored over the recombination reaction, particularly outside the lamp where reversal of Reactions (4) and (5) by photosensitization or direct photolysis is not possible.

If Reactions (1) and (5) are assumed to be the main reactions responsible for disposing of the atoms formed in the primary process, the mechanism for the

photosensitized decomposition of nitric oxide would appear to be:



Two major points of difference exist between earlier studies and the present investigation.

The fact that Flory and Johnston (2) observed no photosensitized decomposition is rather puzzling. An explanation may possibly be found in their description of the light source which they used; "Most of the experiments were done with a quartz mercury arc which was relatively weak in unreversed  $\lambda 2537$  radiation". If most of the  $2537 \text{ \AA}$  radiation was reversed it is difficult to understand how any of their  $1849 \text{ \AA}$  radiation could be unreversed. Line reversal would of course eliminate any possibility of a photosensitized reaction.

Noyes (11) found that the decomposition of nitric oxide was a process photosensitized by  $2537 \text{ \AA}$  resonance radiation. He used a medium pressure arc cooled by water, and in several experiments employed a corex reaction vessel. These experimental conditions preclude the possibility of reaction by  $1849 \text{ \AA}$  radiation. However medium pressure arcs are rich in lines for the whole mercury spectrum and the possibility of stepwise radiation cannot be excluded. It is therefore tentatively suggested that the photosensitized decomposition which Noyes observed and ascribed to  $6^3P_1$  mercury atoms was actually due to the presence of  $7^3S_1$  mercury atoms produced through the absorption of  $4047 \text{ \AA}$  radiation by  $6^3P_0$  mercury atoms or of  $4359 \text{ \AA}$  radiation by  $6^3P_1$  mercury atoms.

In the present investigation a low pressure mercury-rare gas discharge lamp was used and the lines at  $4047 \text{ \AA}$  and  $4359 \text{ \AA}$  would be weak. For this reason little or no decomposition would be expected by way of stepwise radiation.

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# SYNTHESIS OF 1,1,1-TRICHLORO-2,2-BIS-(*p*-CYANOPHENYL)-ETHANE<sup>1</sup>

BY YVON PERRON AND ROGER BARRÉ

## ABSTRACT

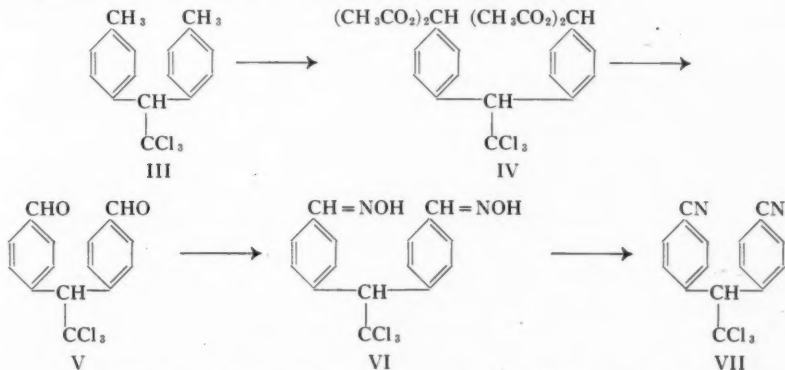
The synthesis of 1,1,1-trichloro-2,2-bis-(*p*-cyanophenyl)-ethane was carried out with the condensation product of chloral and toluene as starting material. This product was converted, through the corresponding tetraacetate, to 1,1,1-trichloro-2,2-bis-(*p*-aldehydophenyl)-ethane which in turn reacted with hydroxylamine to give the dioxime. The subsequent dehydration of the latter gave rise to the desired dinitrile. The corresponding dichloro derivatives of the oxime and nitrile were also prepared.

The first attempt to prepare 1,1,1-trichloro-2,2-bis-(*p*-cyanophenyl)-ethane was made by Hepp and Spiess (2). According to their procedure, the condensation of chloral with benzonitrile was made, using sulphuric acid as condensing agent; a compound having Structure I was obtained.



Later, Weizmann and co-workers (3) started with 1,1,1-trichloro-2,2-bis-(*p*-aminophenyl)-ethane (II) which was diazotized and the resulting diazo compound was treated with cuprous cyanide; an oil was obtained which could not be crystallized. Similarly, unsuccessful results were obtained in our laboratory when we followed the same procedure.

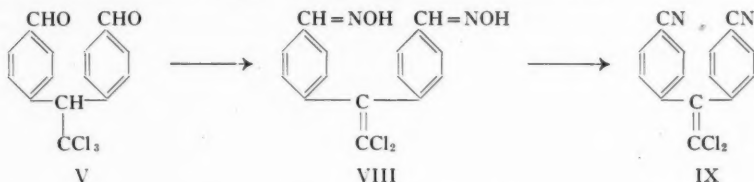
The synthesis of 1,1,1-trichloro-2,2-bis-(*p*-cyanophenyl)-ethane was successfully carried out, when the condensation product of chloral and toluene was used as starting material. This condensation product (III) was submitted to the treatments outlined in the following scheme of equations:



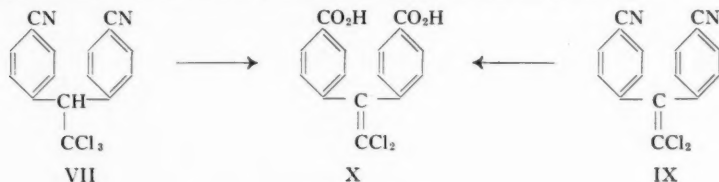
<sup>1</sup> Manuscript received in original form January 12, 1950, and, as revised, November 23, 1951. Contribution from l'Institut de Chimie, Université de Montréal, Montréal, Que.

1,1,1-Trichloro-2,2-bis-(*p*-tolyl)-ethane (III), dissolved in a mixture of acetic acid and acetic anhydride, was oxidized with the aid of chromium trioxide to the tetraacetate (IV). This last compound, upon acid hydrolysis, gave rise to 1,1,1-trichloro-2,2-bis-(*p*-aldehydophenyl)-ethane (V). This aldehyde reacted with hydroxylamine to give the corresponding dioxime (VI) which, on elimination of two molecules of water by treatment with acetic anhydride or thionyl chloride, formed the expected dinitrile (VII).

When the Compound V was treated with hydroxylamine, in an alkaline medium, one molecule of hydrogen chloride was eliminated and 1,1-dichloro-2,2-bis-(*p*-aldoximinophenyl)-ethylene (VIII) was obtained. Dehydration of this ethylenic dioxime, by treatment with thionyl chloride or acetic anhydride, gave rise to 1,1-dichloro-2,2-bis-(*p*-cyanophenyl)-ethylene (IX).



Both the dinitrile, VII, and the ethylenic dinitrile, IX, upon alkaline hydrolysis, produced 1,1-dichloro-2,2-bis-(*p*-carboxyphenyl)-ethylene (X).



#### EXPERIMENTAL

##### *Tetraacetate of 1,1,1-Trichloro-2,2-bis-(p-aldehydophenyl)-ethane*

A 1000 ml. three-necked flask was equipped with a mechanical stirrer and thermometer, while the third neck was closed with a stopper and used for the addition of reagents. The reaction flask was immersed in an ice-salt bath and 1,1,1-trichloro-2,2-bis-(*p*-tolyl)-ethane (25 gm.), prepared according to the procedure outlined by Fischer (1), was introduced together with acetic anhydride (300 cc.) and glacial acetic acid (100 cc.). The resulting solution was cooled to 0°C. and concentrated sulphuric acid (40 cc.) was added slowly, from a dropping funnel, with cooling and stirring. After completion of the addition, the solution was cooled again to 0°C. and then chromic anhydride (50 gm.) was added, in small portions, at such a rate that the temperature did not rise above 5°C. The stirring was continued for 10 min. after all the chromium trioxide had been added. The contents of the reaction flask was poured on crushed ice contained in a large beaker. The precipitate was filtered off and washed with cold water until the washings were colorless. The solid was suspended in a solution



of cold 2% sodium hydroxide (200 cc.) and the suspension was mechanically stirred for 10 min. The product was filtered off, washed several times with small quantities of cold water, and recrystallized from water-dioxane. After two recrystallizations, the crystals consisted of colorless elongated plates containing a molecule of dioxane of crystallization. On heating, *in vacuo* at the temperature of boiling water, the solvent of crystallization was eliminated and the dried product melted at 122°C. Yield, 70%. Calc. for  $C_{24}H_{23}O_8Cl_3 \cdot C_4H_8O_2$ : C, 53.03; H, 4.90; Cl, 16.81; dioxane, 13.89%. Found: C, 53.01; H, 4.95; Cl, 16.80; dioxane, 13.77%.

*1,1,1-Trichloro-2,2-bis-(p-aldehydophenyl)-ethane*

The tetraacetate (15 gm.) was dissolved in a boiling 50% water-ethanol mixture (250 cc.), and concentrated sulphuric acid (10 cc.) was added cautiously. The resulting solution was refluxed for 30 min. The hot solution was then filtered and allowed to cool slowly; crystals of the aldehyde deposited. The filtered crystalline product was recrystallized from boiling ethanol-water from which it separated as an almost white crystalline solid, melting at 148°C. (dec.). Yield, 98%. Calc. for  $C_{16}H_{11}O_2Cl_3$ : C, 56.22; H, 3.22; Cl, 31.18%. Found: C, 56.28; H, 3.30; Cl, 31.20%.

*1,1,1-Trichloro-2,2-bis-(p-aldoximinophenyl)-ethane*

To a solution of 1,1,1-trichloro-2,2-bis-(p-aldehydophenyl)-ethane (10 gm.) in ethanol (100 cc.), hydroxylamine hydrochloride (6.1 gm.) and anhydrous sodium acetate (7.2 gm.) were added. The resulting mixture was refluxed gently for one hour. After cooling, the sodium chloride formed during the reaction was filtered off. The alcoholic filtrate was diluted with water to the point of incipient turbidity. The solution, while standing overnight in the cold, deposited a crop of crystals. These were recrystallized from ethanol-water from which were obtained colorless rods, containing water of crystallization, m.p. 126°C. On heating *in vacuo*, at the temperature of boiling water, the molecule of water was eliminated; the dried product melted at 139°C. Yield, 60%. Calc. for  $C_{16}H_{13}O_2N_2Cl_3 \cdot H_2O$ : C, 49.30; H, 3.85; Cl, 27.36; N, 7.18;  $H_2O$ , 4.62%. Found: C, 49.24; H, 3.90; Cl, 27.32; N, 7.21;  $H_2O$ , 4.30%.

*1,1,1-Trichloro-2,2-bis-(p-cyanophenyl)-ethane*

Thionyl chloride was added slowly from a dropping funnel to anhydrous 1,1,1-trichloro-2,2-bis-(p-aldoximinophenyl)-ethane (5 gm.), until evolution of sulphur dioxide and hydrogen chloride had ceased. Water was then added cautiously to destroy the excess thionyl chloride. A yellow gum separated from which the supernatant liquor was decanted. The gummy residue was washed several times with cold water and subsequently dissolved in 70% acetic acid. The resulting solution was decolorized with charcoal, filtered, and the filtrate was allowed to cool. The nitrile which separated, after recrystallizations from 70% acetic acid, consisted of colorless plates, melting at 149°C. Yield, 80%. Calc. for  $C_{16}H_9N_2Cl_3$ : C, 57.22; H, 2.68; N, 8.34; Cl, 31.74%. Found: C, 57.15; H, 2.74; N, 8.36; Cl, 31.70%.

Alternatively, acetic anhydride instead of thionyl chloride could be used as dehydrating agent, according to the following procedure.



1,1,1-Trichloro-2,2-bis-(*p*-aldoximinophenyl)-ethane (4.2 gm.) was dissolved in acetic anhydride (50 cc.) and the resulting solution refluxed for two hours. It was then filtered to remove a small quantity of insoluble impurities, and the filtrate concentrated to half-volume by distillation. The excess acetic anhydride was hydrolyzed by adding water dropwise to the boiling solution. The yellow solution so obtained was boiled with a little charcoal to remove the coloring material, filtered, and allowed to cool. The crystalline product thus obtained was recrystallized from 70% acetic acid from which it separated as colorless plates, melting at 149°C. Yield, 70%.

*1,1-Dichloro-2,2-bis-(p-aldoximinophenyl)-ethylene*

To a solution of 1,1,1-trichloro-2,2-bis-(*p*-aldehydophenyl)-ethane (1 gm.) in 95% ethyl alcohol (50 cc.), hydroxylamine hydrochloride (1 gm.) and potassium hydroxide (1.5 gm.) were added. The resulting mixture was refluxed gently for 30 min., after which it was filtered from the potassium chloride formed during the reaction. The filtrate was acidified with concentrated hydrochloric acid and subsequently diluted with an equal volume of water. On cooling, crystals of the ethylenic dioxime deposited. After recrystallization from 50% ethanol, the crystalline product consisted of slightly yellow plates, melting at 187-188°C. Yield, 80%. Calc. for  $C_{16}H_{12}O_2N_2Cl_2$ : C, 57.28; H, 3.58; Cl, 21.19; N, 8.35%. Found: C, 57.21; H, 3.63; Cl, 21.12; N, 8.40%.

*1,1-Dichloro-2,2-bis-(p-cyanophenyl)-ethylene*

1,1-Dichloro-2,2-bis-(*p*-aldoximinophenyl)-ethylene (1 gm.) was treated dropwise with thionyl chloride, until the evolution of sulphur dioxide and hydrogen chloride had ceased. The unreacted thionyl chloride was decomposed by the cautious addition of water from a dropping funnel. This caused the separation of a yellow gum from which the supernatant liquor was decanted. The residual gum was washed several times with cold water and finally dissolved in boiling 70% acetic acid. The resulting solution was refluxed with charcoal, filtered, and allowed to cool. On cooling, a crystalline product separated which, after recrystallization from 70% acetic acid, was obtained as colorless rectangular plates, melting at 139°C. Yield, 85%. Calc. for  $C_{16}H_8N_2Cl_2$ : C, 64.21; H, 2.67; Cl, 23.74; N, 9.36%. Found: C, 64.16; H, 2.75; Cl, 23.67; N, 9.30%.

*1,1-Dichloro-2,2-bis-(p-carboxyphenyl)-ethylene*

A mixture of 1,1-dichloro-2,2-bis-(*p*-cyanophenyl)-ethylene (1 gm.), 10% sodium hydroxide solution (40 cc.), and 95% ethyl alcohol (10 cc.) was refluxed for three hours or until a clear solution was obtained. The alcohol was then distilled off and the residual aqueous solution acidified with a 10% sulphuric acid solution to liberate the free acid. The precipitated carboxylic acid was filtered off and washed with small portions of cold water. It was then dissolved in boiling 50% ethanol and the resulting solution was decolorized with charcoal. On cooling, 1,1-dichloro-2,2-bis-(*p*-carboxyphenyl)-ethylene crystallized out as colorless needles, melting at 278°C. Yield, 60%. Calc. for  $C_{16}H_{10}O_4Cl_2$ : C, 56.97; H, 2.96; Cl, 21.06%; mol. wt., 337. Found: C, 56.85; H, 2.99; Cl, 21.15%; mol. wt., 339.

Similarly, this ethylenic carboxylic acid was prepared by alkaline hydrolysis of 1,1,1-trichloro-2,2-bis-(*p*-cyanophenyl)-ethane, from which a molecule of hydrogen chloride was eliminated during the reaction of hydrolysis. The procedure employed was the same as the one described above for the alkaline hydrolysis of the corresponding dichloroethylenic dinitrile.

#### ACKNOWLEDGMENT

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# THE SYNTHESIS OF DIBENZ[*a,c*][1,3]CYCLOHEPTADIENE-5,7-DIONE<sup>1</sup>

BY HAROLD W. LUCIEN<sup>2</sup> AND ALFRED TAURINS

## ABSTRACT

The synthesis of dibenz[*a,c*][1,3]cycloheptadiene-5,7-dione (I), a new member of the dibenz[*a,c*][1,3]cycloheptadiene (II) series, has been accomplished by (1) the condensation of diethyl diphenate and ethyl acetate with alkaline catalysts, (2) the reaction of diphenoyl chloride and sodiomalonic ester, and (3) the condensation of diphenic anhydride and malonic ester with zinc chloride. In addition to the (I), these reactions afford comparable amounts of 2,2'-diacetyl biphenyl (XIII). It has been possible to establish the identity of (I) from the carbonyl and enolic derivatives and products obtained in reactions of hydrolysis, oxidation, and reduction.

## INTRODUCTION

The interest in dibenz[*a,c*][1,3]cycloheptadiene (II) and its derivatives developed as a result of two trends of investigation. One group of workers was concerned with the extension of classical reactions which would produce substances containing homocyclic seven-membered rings. A second group of scientists had the objective to synthesize compounds related to DL-colchicol methyl ether, and dihydrodeaminocolchicol methyl ether, degradation products of colchicine. In the first group properly fall the early investigations of Kenner and Turner (19, 20) who cyclized 2,2'-biphenyl derivatives by several methods and obtained a carboxylic acid, an amine, and a ketone with the functional groups at the sixth atom of (II). To the same group belong reactions of cyclization of biphenyl dialdehyde acetal (26), and of 2-bromo-5-nitroacetophenone (7).

Taurins (25) condensed diphenic anhydride with 2,4-dimethylpyridine to obtain 6-(4-methyl-2-pyridyl)-dibenz[*a,c*][1,3]cycloheptadiene-5,7-dione (III), a representative of a new class of compounds, diphenones, containing a ring system of (I). This reaction was also extended to other 2-methylpyridines and 2-methylquinolines (25, 4).

As Barton, Cook, and Loudon (3) pointed out, a degradation product of colchicine, deamino colchicol methyl ether, is a derivative of dibenz[*a,c*][1,3]cycloheptadiene. Cook, Dickson, and Loudon (12) prepared for the first time a hydrocarbon, dibenz[*a,c*][1,3]cycloheptatriene (V), by treatment of N-acetylamine (IV) with phosphorus pentoxide in xylene; in the same series of experiments two ketones (VI, VII) were prepared. Almost at the same time the synthesis of (V) was announced by Lettré (21).

Rapoport and Williams (23) cyclized  $\beta$ -[2-(2'-cyanophenyl)]-phenylpropanitrile to obtain (II) and a number of its derivatives. Rapoport, Williams, and Cisney (24) extended this method to the methoxy substituted series of (II) to synthesize dihydrodeaminocolchicol methyl ether.

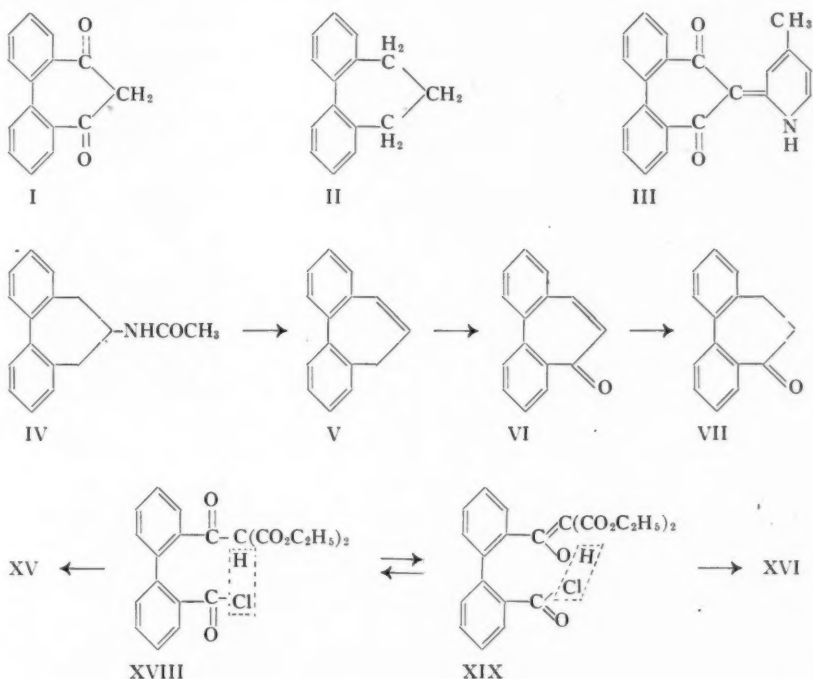
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The monoketone (VI) and its tetramethoxy derivative was obtained by Buchanan, Cook, Loudon, and MacMillan (9) using a cycle of reactions discovered by Criegee, Marchand, and Wannowius (13). The monoketone (VII) was synthesized by Cook (11) by cyclization of 3-(2-biphenyl)propionyl chloride with hydrogen fluoride as catalyst.

Cook (11) tried to oxidize these monoketones with an acetic acid solution of sodium dichromate to obtain diketones and triketones of (II); however, instead of the expected products, phenanthrene quinone was the only carbonyl compound isolated.



FORMULAE SCHEME I.

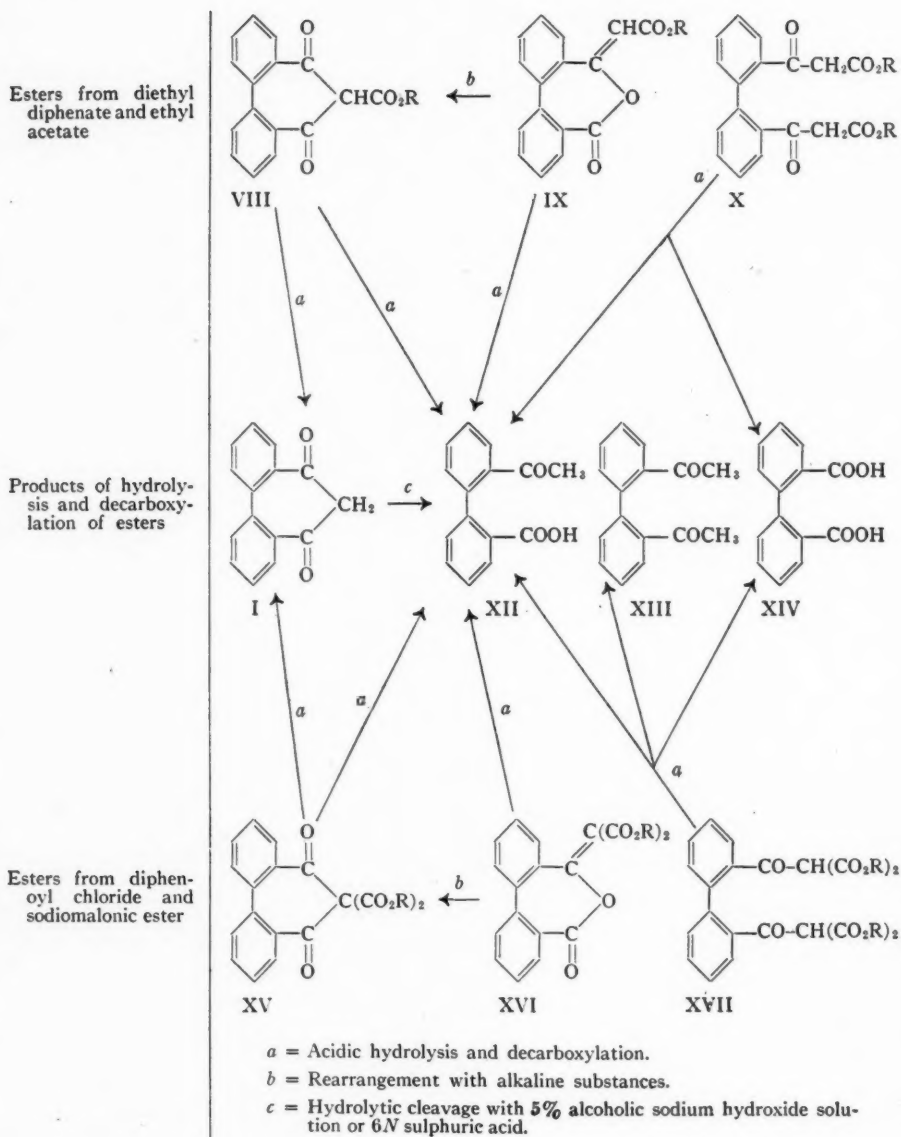
The objective of the present work was to study the synthesis and properties of dibenz[*a, c*][1,3]cycloheptadiene-5,7-dione in order to provide a detailed knowledge of the parent ring system of pyridodiphenones.

#### Preparation of Intermediates

(a) *Diphenic Acid* (XIV) was prepared by oxidation of crude phenanthrene (90%) via phenanthraquinone (15, 14, 2).

(b) *Diphenic Anhydride* was prepared by refluxing of (XIV) with acetic anhydride in ratio 1:2 by weight (16, 5).

TABLE I  
REACTIONS OF THE ESTERS



(c) *Diethyl Diphenate* was obtained by esterification of (XIV) in absolute ethanol using either hydrogen chloride (18) or sulphuric acid as a catalyst. A new method for synthesis of diethyl diphenate was developed using a reaction between diphenoyl chloride and sodium ethoxide.

(d) *Diphenoyl Chloride* was synthesized by heating of (XIV) with pure phosphorus pentachloride and removal of phosphorus oxychloride by distillation in vacuum. The crude diphenoyl chloride was purified by recrystallization from di-isopropylether and obtained in beautiful colorless crystals.

#### *Condensation of Diethyl Diphenate and Ethyl Acetate*

In attempts to close a seven-membered ring fused with diphenyl system by a method similar to that employed by Wislicenus (27) to prepare 1,3-indandione, three variations of the ester condensation were used. These included the condensation of diethyl diphenate and ethyl acetate with sodium metal, sodium ethoxide, and triphenylmethyl sodium. Theoretically, this condensation could produce three main  $\beta$ -ketoesters or their sodium derivatives: (VIII), (IX), and (X). Although in no instance were these esters isolated, they were formulated on the basis of the final products which were isolated after the hydrolysis and decarboxylation. The esters were viscous liquids with high boiling points, and they did not crystallize. Usually they were hydrolyzed and decarboxylated into a mixture of three ketocompounds (I), (XII), and (XIII) which were separated by chemical method.

Using three different basic catalysts in the condensation of diethyl diphenate with ethyl acetate the following yields of (I) were obtained: with sodium metal -9%, sodium ethoxide -13%, triphenylmethylsodium -25%.

The amounts of the isolated 2,2'-diacetyl biphenyl (XIII) was approximately 10%; this indicates that its mother substance (X) is a principal competition product. This observation is contrary to the belief that the seven-membered ring forms with great facility.

The isolation of diphenic acid from the reaction products accounts in part for the low yields of condensation products. The only logical explanation of the formation of diphenic acid is the alkaline cleavage of the  $\beta$ -ketoesters.

Approximately 50% of the condensation products remained as highly viscous liquid which could not be distilled or crystallized. These products could be only converted into diphenic acid by heating with sodium hydroxide.

#### *Condensation of Diphenoyl Chloride with Malonic Ester*

The condensation of diphenoyl chloride with sodiomalonic ester was carried out either in the absence of solvents or in benzene solution. Using methods of crystallization and fractional distillation in vacuum three different ketoesters, (XV), (XVI), and (XVII), were isolated as the reaction products. The formation of the ester (XV) was expected as a result of the elimination of elements of hydrogen chloride from the first simplest intermediate (XVIII); however, this intermediate was apparently very strongly enolized to the substance (XIX), which would lead to the formation of enol-lactone (XVI). Enolization was

facilitated by the excess of sodiomalonic ester. This is reminiscent of Claisen's experiment with benzoylacetone (10).

Diphenoylidenyl malonic ester (XVI) can be partially rearranged into (XV) by sodium ethoxide in absolute ethanol; the principal product of this reaction is 2-(2-carbethoxyphenyl)-benzoylmalonic ester (XX).

In the condensation of diphenoyl chloride with monosodiummalonic ester in benzene solution the crude reaction product was hydrolyzed and decarboxylated with 6 *N* sulphuric acid and the water-acid solution extracted with ether. From the ether solution the (XII) was extracted with sodium bicarbonate solution and the (I) with sodium hydroxide solution; the yield of (I) was 9-10%. The (XIII) remained in the ethereal solution.

Better yields of the (I) were obtained by reaction of disodiummalonic ester with diphenoyl chloride in benzene solution. The crude esters resulting from the condensation could be separated by fractional distillation in vacuum and the yield of the (I) was increased to 25-30%.

#### *Condensation of Diphenic Anhydride and Malonic Ester*

The condensation of diphenic anhydride and malonic ester with zinc chloride was carried out for six hours at 135-140° by heating in an oil bath. The products isolated from the reaction mixture suggested the formation of (XV) in the first step. At the temperature of the reaction, the condensation product underwent further changes to give varying amounts of (I) and (VIII). The ketone (I) could be isolated directly from the condensation products by chemical separation; however, from the standpoint of improving the yield of (I), it was of advantage to hydrolyze and decarboxylate the reaction products prior to the separation of (I). This synthesis afforded the expected 1,3-diketone (I) in yields of the order of 40% of the theoretical quantity.

#### *Hydrolysis and Decarboxylation of $\beta$ -Ketoesters*

Previous workers have used different agents for the hydrolysis and decarboxylation of  $\beta$ -ketoesters to obtain 1,3-diketones. Good success was obtained using a solution of hydrochloric acid, water, and acetic acid in the ratio of 2:1:2 respectively (22), or an aqueous mixture of acetic and sulphuric acids (17). For the same purpose concentrated hydrochloric acid (1), or mixtures of mineral and organic acids (for example, 1% sulphuric acid in glacial acetic acid), were applied (18).

The six  $\beta$ -ketoesters (VIII, IX, X and XV, XVI, XVII) showed great difficulties in the reactions of hydrolysis and decarboxylation owing to their tendency to undergo acidic cleavage to form derivatives of biphenyl. It was found that the esters (XV), (XVI), and (XVII) were much more difficult to hydrolyze than were the esters (VIII), (IX), and (X). There was an additional difficulty that the 1,3-diketone (I) polymerized when heated above about 90° in acidic solutions. Therefore the use of 1% concentrated sulphuric acid in either propionic or acetic acid at the boiling point was not applicable to prepare (I). Moderately concentrated mineral acids—6 *N* hydrochloric acid, 6 *N* sulphuric acid, and 10 *N* sulphuric acid—were somewhat more promising, but the formation of (I) was slow.



To accomplish the ketonic hydrolysis of (XV) at room temperature various concentrations of sulphuric and hydrochloric acids were used. It was found experimentally that hydrolysis with 70-80% aqueous sulphuric acid at room temperature for a period of three or four days, followed by decarboxylation at increased temperature (about 100°) for several hours, favored the production of (I) with minimum side reactions. The yield of (I) obtained under optimal conditions of acid concentration and decarboxylation temperature was approximately 20%.

Hydrolysis of (XV) with either dilute (0.01 *N*) aqueous or alcoholic sodium hydroxide produces at first dibenz[*a, c*][1,3]cycloheptadiene-5,7-dione-6,6-dicarboxylic acid which on refluxing with the reagents undergoes acidic cleavage to form diphenic acid. This was proved by determination of saponification equivalents of (XV) and isolation of the dicarboxylic acid.

#### *Properties and Derivatives of (I)*

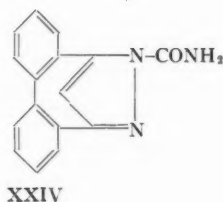
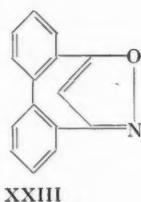
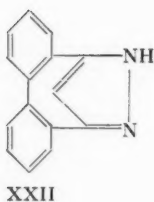
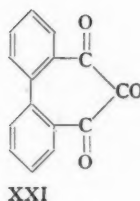
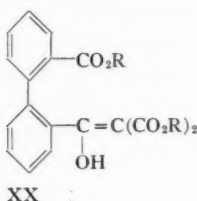
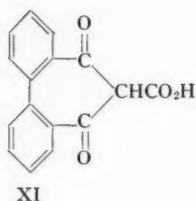
(I) can be isolated as bright yellow crystals which melt at 48-52°. It is very soluble in the ordinary organic solvents and aqueous sodium hydroxide solution. (I) dissolves to the extent of approximately 1.5% in 80% sulphuric acid. It is not possible to recover (I) by extraction with organic solvents once it has dissolved in the acidic solution, although the solution shows reactions of (I). When the solution is evaporated to dryness, only (XII) can be isolated.

(I) can be separated from the nonhydroxylic solvents as an amorphous yellow powder. It can be partially crystallized from a mixture of light petroleum and benzene. Once dissolved in alcohols, especially methanol, or ethanol, it separates as a viscous amber-colored liquid, which can be solidified by removing the last traces of solvents under diminished pressure.

When the dry compound (I) was heated as high as 120° no changes were observed to occur. However, it evidently underwent polymerization when heated above 80-90° in aqueous solution.

It was found that the product separated from the aqueous solutions of (I) as well as from the aqueous solvents melted at 86-92°. The available data suggested that it may be possible for the 1,3-diketone (I) to exist as a monohydrate. On distillation of the monohydrate of (I) 2<sup>1</sup>-acetyl-2-biphenyl-carboxylic acid (XII) resulted. By distillation of (I) obtained from strictly anhydrous, non-hydroxylic solvents only polymeric residues were obtained. Although small yields were realized, it was possible to reduce (I) to dibenz[*a, c*][1,3]cycloheptadiene (II) by Clemmensen method. (II) had the m.p. 53-56°, which was in agreement with a value reported in literature (23).

Selenium dioxide in glacial acetic acid oxidizes (I) to triketone (XXI). This triketone was also obtained when excess of bromine water was added to an alcoholic solution of the diketone (I). Potassium dichromate (in glacial acetic acid) oxidizes (I) to diphenic acid. One or both hydrogen atoms of the methylene group in (I) can be substituted by bromine. The monobromo derivative can be prepared by adding bromine water to an alcoholic or acid solution of (I). Excess of bromine gives triketone, probably through dibromide and gem. diol.



FORMULAE SCHEME II.

The dibromo derivative was prepared by adding the theoretical quantity of anhydrous bromine in chloroform to a solution of (I).

(I) sometimes forms more than one derivative with carbonyl reagents. Hydrazine produces a monohydrazone and a pyrazole derivative (XXII). Hydroxylamine or semicarbazide form with (I) products which are not mono- or dicarbonyl derivatives; the nitrogen determination and a negative qualitative reaction with ferric chloride suggested that these products were an isoxazole (XXIII) and a pyrazole (XXIV) derivatives respectively.

Derivatives of the enolic form of (I) were prepared with  $\alpha$ -naphthylisocyanate to give an  $\alpha$ -naphthylurethane (XXV), benzene diazonium chloride, and a copper salt with cupric acetate.

#### EXPERIMENTAL PART

##### *Diphenoyl Chloride*

Phosphorus pentachloride (44.8 gm. (0.215 mole)) was placed in a 250 ml. flask and heated at 100° for one hour at reduced pressure to remove any phosphorus trichloride or phosphorus oxychloride. The flask was then detached from the reduced pressure system, 44.8 gm. (0.2 mole) of finely powdered, oven-dried (110°) diphenic anhydride was added. The flask was immersed in an oil bath at 145-150°. After a few minutes, the reaction mixture became liquid and a lively reaction took place. The mixture was heated for two hours after which the flask was again connected to the reduced pressure distillation system. The temperature of the bath was allowed to fall to 125-130° and suction was gradually applied. When most of the phosphorus oxychloride had been distilled (20-22 ml.), the flask was cooled. A faintly yellow product solidified. This crude diphenoyl chloride was best purified by recrystallization from di-isopropyl

ether. Diphenoyl chloride was obtained in beautiful white tetragonal crystals which weighed 50 gm. (90% yield) and melted at 97-98°.

#### *Diethyl Diphenate*

##### *(a). By a Modification of Hummel's Method*

In a 500 ml. three-necked flask, fitted with mercury-sealed stirrer, a condenser, and an inlet for anhydrous hydrogen chloride, were placed 121.1 gm. (0.5 mole) of diphenic acid and 230 gm. (5 moles) of absolute ethanol. The hydrogen chloride gas was conducted into the reaction mixture till the saturation. The reaction mixture was heated on the steam bath for five hours, and then 200 ml. of alcohol distilled off. The cooled residue was dissolved in 200 ml. of ethyl ether. The ether solution was washed with two 50 ml. portions of water, followed by three 50 ml. portions of 5% sodium hydroxide and then two 50 ml. portions of water. After drying the ether was distilled off. On standing, the thick residue crystallized. By recrystallization of diethyl diphenate 94-100 gm. (64-67%) of rhombic crystals, m.p. 42-43°, was obtained. Some of these crystals measured as much as  $1 \times 1 \times \frac{3}{4}$  in.

##### *(b). By the Reaction of Diphenoyl Chloride and Sodium Ethoxide*

A mixture of 27.8 gm. (0.1 mole) of diphenoyl chloride and 13.6 gm. (0.2 mole) of sodium ethoxide in 50 ml. of absolute alcohol was heated to reflux on a steam bath for one hour, after which the alcohol was distilled. The diphenic ester was purified as above in Procedure (a). The yield was of order 28-29 gm. (94-97%). Diphenic ester formed a colorless liquid, b.p. 208-209° at 2 mm. It solidified into white crystals, m.p. 42°.

##### *A. Condensation of Esters with Sodium Metal*

A mixture of 158 gm. (1.8 moles) of ethyl acetate, 4.6 gm. (0.2 gm.-atom) of sodium metal and 29.8 gm. (0.1 mole) of diethyl diphenate was heated at 60-65° for 13 hr. The dark reddish-brown semisolid reaction product was treated with 100 ml. of 95% ethanol in order to destroy small amounts of sodium. The residue was hydrolyzed and decarboxylated by heating with 500 ml. of 2 *N* sulphuric acid at 80-90° until the evolution of carbon dioxide had ceased.

*Dibenz[a, c][1,3]cycloheptadiene-5,7-dione-6-carboxylic acid (XI).*—The hydrolyzate was extracted three times with 50 ml. portions of ether; the organic material was dissolved in the combined ether extracts ( $E_1$ ) and the resulting solution was washed three times with 25 ml. portions of water. The ethereal solution ( $E_1$ ) was then extracted with three 25 ml. portions of 5% sodium hydroxide solution ( $W_1$ ) and acidified with dilute hydrochloric acid (1:4); this caused a product of tarlike consistence to separate. The residue was dissolved in 100 ml. of a saturated solution of cupric acetate in methanol. The dark green copper salt was filtered by suction, washed with methanol, and decomposed by concentrated hydrochloric acid at 50-60°. The product was recrystallized from acetic acid and water; white crystals, m.p. 238-240°; yield 4 gm. (9%).

Anal. Calcd. for  $C_{16}H_{10}O_4$ : C, 72.19; H, 3.79%; NE, 266.2.

Found: C, 71.97; H, 3.61%. NE, 265.9.

*Dibenz[a, c][1,3]cycloheptadiene-5, 7-dione (I) by decarboxylation of (XI).*—2.7 gm. (0.01 mole) of (XI) was heated at 120°; it melted and a lively evolution of carbon dioxide took place. The residue was a brittle amberlike solid, m.p. 48–52°. It weighed 2.7 gm. (98%).

Anal. Calcd. for  $C_{15}H_{10}O_2$ : C, 80.91; H, 4.11%; MW, 222.2.

Found: C, 80.88; H, 4.03%; MW, 212.7.

*2<sup>1</sup>-Acetyl-2-biphenylcarboxylic acid (XII).*—The alcoholic solution which remained after the separation of the copper salt of (XI) was made alkaline with 50 ml. of 10% sodium hydroxide and copper hydroxide filtered off. The alkaline solution was acidified with acetic acid to such an extent that the solution remained clear. It was decolorized and filtered. Upon cooling, white crystals separated; yield 10 gm. (40%); m.p. 121–122°.

Anal. Calcd. for  $C_{16}H_{12}O_3$ : C, 75.01; H, 5.04%; NE, 240.2.

Found: C, 74.99; H, 5.00%; NE, 239.2.

*The 2, 4-dinitrophenylhydrazone of (XII).*—A mixture of 0.2 gm. of (XII), 0.2 gm. of 2,4-dinitrophenylhydrazine and 10 ml. of 95% ethanol was refluxed for one-half hour; 0.5 ml. of concentrated hydrochloric acid was added and the mixture was refluxed for an additional 15 min. Upon cooling, bright orange needles formed. The derivative was recrystallized from alcohol; m.p. 276–278°.

Anal. Calcd. for  $C_{21}H_{16}O_6N_4$ : N, 13.34%. Found: N, 13.17%.

*2, 2'-Diacetylbiiphenyl (XIII).*—The ethereal solution ( $E_1$ ) was washed three times with 25 ml. portions of water and then dried over calcium chloride. Fractional precipitation of a pale yellow solid from the ether solution could be effected by the addition of petroleum ether. The precipitate was recrystallized from 95% ethanol and water was added until the boiling solution became slightly turbid. Upon cooling, fine white needles of (XIII) was obtained (3 gm. or 12% based on diethyl diphenate), m.p. 84–85°.

Anal. Calcd. for  $C_{16}H_{14}O_2$ : C, 80.75; H, 5.94%.

Found: C, 80.71; H, 5.96%.

*The dioxime of (XIII).*—To a solution of 0.5 gm. of hydroxylamine hydrochloride in 3 ml. of water was added 0.2 gm. of (XIII). After the dissolving of 0.3 gm. of sodium hydroxide in the solution, ethanol was added until a clear solution resulted. The mixture was heated on a steam bath for five minutes and the dioxime precipitated by pouring the reaction mixture into 5 ml. of concentrated hydrochloric acid. White crystals crystallized from alcohol, m.p. 210–212° (dec.).

#### B. Condensation of Esters with Sodium Ethoxide

Alcohol free sodium ethoxide was prepared by the reaction of 6.9 gm. (0.3 gm.-atom) of sodium metal and 150 ml. absolute alcohol and evaporation of excess of alcohol in nitrogen stream. Diethyl diphenate (29.8 gm. (0.1 mole)) was added to the sodium ethoxide, followed by addition of 20 gm. of ethyl acetate. The mixture was heated under reflux with stirring for two hours. The remaining ethyl acetate (138 gm.) was added over a period of three hours. The reaction mixture was then heated for an additional 12 hr. Alcohol and unreacted esters were distilled off under gradual increase of temperature to 175–180°, at reduced

pressure. The residue was dissolved in a mixture of 150 ml. each of ethyl ether ( $E_2$ ) and water ( $W_2$ ).

The ether fraction ( $E_2$ ) was dried over calcium chloride and ether distilled off. The residue was heated at the boiling point with 6 *N* sulphuric acid until the evolution of carbon dioxide ceased. The mixture was cooled and extracted three times with 20 ml. portions of ether ( $E_3$ ). The ether solution ( $E_3$ ) was extracted with three 20 ml. portions of saturated sodium bicarbonate solution ( $W_3$ ). After being washed with water, the ether solution was extracted three times with 20 ml. portions of 5% sodium hydroxide solution ( $W_4$ ). The ether layer was washed with water and dried over anhydrous magnesium sulphate. From this solution only (XIII) was obtained.

*Dibenz[a, c][1,3]cycloheptadiene-5,7-dione monohydrate (Ia).*—The alkaline solution ( $W_2$ ) was decarboxylated by heating with 6*N* sulphuric acid. The mixture was cooled and neutralized with sodium hydroxide solution ( $W_5$ ); it was extracted thrice with 20 ml. portions of ether ( $E_5$ ). From the ether solution 3 gm. of (XIII), m.p. 84–85°, was isolated. The alkaline solution ( $W_5$ ) was saturated with carbon dioxide. This caused a dark yellow precipitate to form. The mixture was evaporated to 50 ml., cooled, and extracted three times with 20 ml. portions of ether ( $E_4$ ). Acidification of the aqueous solution afforded 1 gm. of diphenic acid, m.p. 227–229°. Evaporation of the ether solution ( $E_4$ ) gave a dark-brown residue (Ia), m.p. 85–95°. It gave a positive ferric chloride test of enols and a green cupric salt. Only very extensive drying of the substance in Abderhalden apparatus over phosphorus pentoxide at 100° caused a loss of water to form (I). (I) was crystallized from ether solution by fractional precipitation with petroleum ether; m.p. 48–52°. Yield 3 gm. (13%).

*2<sup>1</sup>-Acetyl-2-biphenylcarboxylic acid (XII).*—(a) *By the distillation of (Ia).* Distillation of (Ia) in vacuum yielded a pale yellow liquid, b.p. 168–170° at 0.3 mm., which solidified into pale yellow crystals, m.p. 120–122°. (b). *From the bicarbonate extract ( $W_3$ ).* Acidification of the bicarbonate solution yielded 8 gm. (35%) of (XII), m.p. 120–122°.

#### C. Condensation of the Esters with Triphenylmethylsodium

To a solution of 27.9 gm. (0.105 mole) of triphenylmethylsodium (6) in 500 ml. ether 13.2 gm. (0.15 mole) of ethyl acetate was added. The flask was shaken and 14.9 gm. (0.05 mole) of diethyl diphenate was added slowly. After the vigorous reaction was over the flask was heated at 110–115° for one and one-half hours. The flask was cooled and the ether solution ( $E_6$ ) was extracted with three 50 ml. portions of water ( $W_6$ ). The ether was distilled from the solution ( $E_6$ ). The residue was cooled and 100 ml. of 80% sulphuric acid was added. The mixture was allowed to stand for four days; the flask was heated on a steam bath until the evolution of carbon dioxide ceased (two-three hours). After the cooling of the flask the solution was extracted with three 30 ml. portions of ether ( $E_7$ ).

The ether solution ( $E_7$ ) was washed with three 20 ml. portions of saturated bicarbonate solution and three 20 ml. portions of 10% sodium hydroxide; the



latter solution was washed with ether, decolorized, acidified with 5% hydrochloric acid, and extracted with two 50 ml. portions of ether. The ether extract was dried over anhydrous magnesium sulphate for three days. The solution was concentrated in a test tube and the residue was dried in an Abderhalden apparatus over anhydrous at 100° and 0.1 mm. for 12 hr. The product thus obtained weighed 5-7 gm. (25-30%) and melted at 48-52°. It was identified as (I) by its m.p., analysis, and derivatives. From the corresponding solutions (XII) and (XIII) were obtained by methods which were described previously. The yields of (XII) and (XIII) were 3 gm. (10%) and 4 gm. (17%), respectively.

*D. Condensation of Diphenoyl Chloride and Monosodiummalonic Ester in the Absence of a Solvent*

The mixture of monosodiummalonic ester [prepared from 1.8 gm. sodium metal and 12.8 gm. malonic ester (each 0.08 moles) and 20 ml. of absolute alcohol, and distilling the alcohol in N<sub>2</sub> atmosphere] and 13.9 gm. (0.05 mole) of finely powdered diphenoyl chloride was heated at 100-105° for one hour. The flask was cooled and the residue was dissolved in 95% ethyl alcohol.

*Diphenylidenylmalonic ester (XVI).*—The alcoholic solution of the condensation product was filtrated and the filtrate was heated on a steam bath; the hot solution was titrated with water to slight turbidity. The grayish-white crystals which formed by cooling in an ice-salt bath weighed 11 gm. (60%). The product was recrystallized from benzene; glistening white crystals, m.p. 95°. It did not form a derivative with carbonyl reagents.

Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>6</sub>: C, 68.83; H, 4.95%; SE, 91.58; MW, 366.6.  
Found C, 68.85; H, 4.90%; SE, 90.25; MW, 345.1 (Rast), 360.9 (Beckmann).

*2<sup>1</sup>-Acetyl-2-biphenylcarboxylic acid (XII) by decarboxylation of (XVI).*—3.7 gm. (0.01 mole) of (XVI) and 15 ml. of 80% sulphuric acid were heated on a steam bath until the evolution of carbon dioxide ceased. The flask was cooled in an ice-salt bath. The precipitate was recrystallized from acetic acid and water. The straw-colored crystals which weighed 1.9 gm. (79%) and melted at 121-122° were identified as (XII) by the melting point and mixed melting point data.

*E. Condensation of Diphenoyl chloride and Disodiummalonic Ester in Benzene Solution*

Diphenoyl chloride (27.8 gm. (0.1 mole)) in 125 ml. of anhydrous benzene was added to a sample of disodiummalonic ester, which was prepared from 14.4 gm. (0.2 mole) of dry sodium ethoxide and 16.1 gm. (0.1 mole) of malonic ester in 120 ml. of benzene. The addition lasted for one hour and the reaction was exothermic. The flask was heated on an oil bath for three hours at 80-85°. Then it was cooled and the benzene solution was washed with three 50 ml. portions of 1 N sulphuric acid and then three times with water. The benzene solution was dried over anhydrous magnesium sulphate. After 12 hr. the solution was concentrated in a 50 ml. pear-shaped flask provided with a fractionating column. The following fractions were collected during a typical distillation.

Fraction No.	B.p.	Pressure, mm.	Weight, gm.
1	94—100°	15	3
2	115—134°	0.9	4
3	145—156°	0.7	8
4	143—150°	0.3	11
5 (residue)			

Refractionation of the *fraction No. 1* afforded malonic ester, boiling point, 92–93° at 15 mm.; refractive index,  $n_D^{25}$ , 1.4145. *Fraction No. 2* partially crystallized immediately after distillation. The substance was identified as diethyl diphenate, melting point 42° (from benzene and petroleum ether).

*sym-Diphenoxymalonic ester (XVII).*—*Fraction No. 3* was a viscous yellow liquid which crystallized only after long standing (two-four months). These crystals melted at 46–48°. The fraction was redistilled and 3.1 gm. collected. The substance gave a red color with alcoholic ferric chloride. It dissolved in 5% sodium hydroxide solution, but not in a saturated solution of sodium bicarbonate. Anal. Calcd. for  $C_{28}H_{30}O_{10}$ : C, 64.91; H, 5.75%. Found: C, 64.88; H, 5.80%.

*2,2'-Diacetylbiphenyl (XIII) by decarboxylation of (XVII).*—1.0 gm. of (XVII) and 15 ml. of 4 *N* sulphuric acid were heated on a steam bath until the evolution of carbon dioxide stopped. The solid substance was recrystallized from methanol–water and obtained as white crystals (0.2 gm.), m.p. 84–85°. *Fraction No. 4*, a brownish-yellow viscous liquid, was decarboxylated with hydrochloric acid. For each gram of the fraction, 1 ml. of concentrated hydrochloric acid and 1.5 ml. of water were used. The mixture was heated at 50° for three days. After that time the temperature was increased to 100°. When the evolution of carbon dioxide ceased, the solution was extracted with ethyl ether ( $E_8$ ). The hydrochloric acid solution was evaporated at reduced pressure. The brown residue weighed 2.7 gm. It was washed with 25 ml. of ether. The ether was combined with the ethereal solution ( $E_8$ ). The pale yellow residue which remained weighed 0.9 gm. It was crystallized from acetic acid and water and identified as (XII), m.p. 120–122°. From the ether solution ( $E_8$ ), 7 gm. of (I) (30%) was isolated, m.p. 48–52°.

*6,6'-Dicarboethoxy-dibenz[a, c][1,3]cycloheptadiene-5,7-dione (XV).*—When fraction No. 4 was refractionated, 8 gm. of a yellow, viscous liquid was obtained. This fraction boiled 185–188° at 0.9 mm. Crystals could not be obtained from the product until it had been standing for approximately two weeks. The density of the liquid was observed to be  $d_4^{25}$ , 1.1325 and refractive index  $n_D^{25}$ , 1.5580. Anal. Calcd. for  $C_{21}H_{18}O_6$ : C, 68.83; H, 4.95%; MR, 104.8; SE, 183.2; MW, 365.3. Found: C, 68.80; H, 4.96%; MR, 104.6; SE, 187.2; MW, 360.1.

*The di-2,4-dinitrophenylhydrazones of (XV).*—A mixture of 0.5 gm. of 2,4-dinitrophenylhydrazine, 0.5 gm. of the ester and 25 ml. of 95% ethanol was refluxed for 15 min. Concentrated hydrochloric acid (1 ml.) was added and the solution was cooled. A bright orange-red precipitate immediately separated.



The product was recrystallized from ethyl alcohol, m.p. 245-247°. Anal. Calcd. for  $C_{33}H_{26}O_{12}N_8$ : N, 15.41%. Found: N, 15.30%.

*The mono-2,4-dinitrophenylhydrazone of (XV).*—The alcohol filtrates from the di-derivative were combined and diluted with water. An orange product was obtained which yielded golden orange flakes after recrystallization from methanol and water, m.p. 179-180°. Anal. Calcd. for  $C_{27}H_{22}O_9N_4$ : N, 10.25%. Found: N, 10.21%.

*F. Condensation of Diphenic Anhydride and Malonic Ester*

A mixture of 44.4 gm. (0.2 mole) of diphenic anhydride, 32 gm. (0.2 moles) of malonic anhydride, and 3 gm. (0.002 mole) of fused zinc chloride was heated on an oil bath at 135-140° for six hours. The brown product was stirred at room temperature with 100 ml. of 80% sulphuric acid. After 12 hr., the stirrer was removed and the flask was stoppered. After two days, the flask was heated at 60-70° until the evolution of carbon dioxide stopped. The decarboxylation mixture was extracted with three 100 ml. portions of ethyl ether. The ether solution was washed with water and then extracted with 5% sodium hydroxide solution. The alkaline extract was acidified and cooled in an ice-water bath. The resulting brown solid, primarily a mixture of (I) and (XI), was washed with cold water and air-dried. The mixture was then placed in a 10 cm. evaporation dish and heated in an oven at 120° for one hour. The product melted at 75-100° and was pyrolyzed with the loss of carbon dioxide. The brittle residue was finely powdered. The product was washed well with 50 ml. of a saturated solution of sodium bicarbonate at 50°. The insoluble product was separated by suction filtration and washed with cold water. The residue was treated with 75 ml. of 5% sodium hydroxide solution. This solution was filtered, decolorized, acidified. The product weighed 7.9 gm. (30-40%) and was identified as (I), m.p. 48-52°.

*The Reactions of (I) with Carbonyl Reagents*

*A. With Hydrazine Hydrate*

(a). *The monohydrazone of (I).*—A mixture of 0.2 gm. of (I) and 0.5 ml. of 80% hydrazine hydrate was evaporated to dryness. The residue was dissolved in 2 ml. of water and the solution was made slightly acidic. The product was recrystallized from methanol and water; pale yellow crystals, m.p. 115° (decomp.) The hydrazone produced a red coloration with alcoholic ferric chloride. Anal. Calcd. for  $C_{18}H_{14}ON_2$ : N, 11.85%. Found: N, 11.91%.

(b). *The pyrazole derivative (XXII).*—After heating of the monohydrazone for 15 min. at 215°, the product was recrystallized from methanol and water; yellow crystals, m.p. 207-209°. This product did not give a red coloration with ferric chloride.

Anal. Calcd. for  $C_{18}H_{10}N_2$ : N, 12.84. Found: N, 12.68%.

*B. With Semicarbazide*

*The pyrazole derivative (XXIV).*—0.2 gm. of (I) was added to a solution of 0.5 gm. of semicarbazide hydrochloride and 1 gm. of sodium acetate in 10 ml. of water and 5 ml. alcohol. The solution was heated on a steam bath for 15 min.

and the solution was made slightly acid with hydrochloric acid. The solution was cooled, and the product was filtered; m.p. 175-177°, after recrystallization from methanol and water.

Anal. Calcd. for  $C_{16}H_8ON_3$ : N, 16.29%. Found: N, 16.10%.

*C. With Hydroxylamine*

*The isoxazole derivative (XXIII).*—The condensation product of (I) and hydroxylamine was prepared by the usual procedure and obtained in the form of pale yellow crystals which melted at 217-219°.

Anal. Calcd. for  $C_{15}H_9ON$ : N, 6.39%; Found: N, 6.28%.

*D. With 2,4-Dinitrophenylhydrazine*

A mixture of 0.15 gm. of (I), 0.15 gm. of 2,4-dinitrophenylhydrazine and 3 ml. of glacial acetic acid was refluxed for one hour. The derivative was recrystallized from ethanol and water and melted at 169-170°. The reaction with ferric chloride was negative.

Anal. Calcd. for  $C_{21}H_{14}O_6N_4$ : N, 13.93%. Found: N, 13.84%.

*The Derivatives of the Enol Form of (I)*

*A. The Mono  $\alpha$ -naphthyl-urethane of (I)*

A mixture of 0.2 gm. of (I) and four drops of  $\alpha$ -naphthylisocyanate was heated at 105-110° for one-half hour. The product which formed was recrystallized from methanol and water; pale yellow plates, m.p. 154-155°. It produced a red color with ferric chloride.

Anal. Calcd. for  $C_{26}H_{14}O_3N$ : C, 79.43; H, 4.57; N, 3.57%.

Found: C, 79.01; H, 4.22; N, 3.94%.

*B. 6-Benzeneazo-dibenz[a, c][1,3]cycloheptadiene-5,7-dione*

In 10 ml. of 5% sodium hydroxide was dissolved 1.1 gm. of (I) and the solution was coupled with benzene diazonium chloride (from 0.4 gm. of aniline) at 0°-5°. The mixture turned dark red. A dark reddish-brown product was obtained as a fine granular residue after the recrystallization from alcohol; m.p. 78-86° (decomp.). The reaction with ferric chloride was positive.

Anal. Calcd. for  $C_{21}H_{14}O_2N_2$ : C, 77.38; H, 4.33; N, 8.56%.

Found: C, 76.95; H, 4.47; N, 9.12%.

*C. The Copper Salt*

A methyl alcohol solution containing 0.2 gm. of (I) was treated with 50 ml. of a saturated solution of cupric acetate in methanol. A green precipitate formed immediately. It was washed with methanol and recrystallized from the same solvent. Small olive-green flakes; decompose at 165-168°, without melting.

Anal. Calcd. for  $C_{30}H_{18}O_2$  Cu: Cu, 12.58%. Found: Cu, 12.34%.

*Dibenz[a, c][1,3]cycloheptadiene-5,6,7-trione (XXI)*

A mixture of 2.2 gm. of (I), 1 gm. of resublimed selenium dioxide, and 5 ml. of glacial acetic acid was heated on a steam bath for three hours and filtered. The filtrate was diluted with 20 ml. of water and cooled in an ice-water bath. The residue was dissolved in 5 ml. of glacial acetic acid; the solution was decolorized

and filtered. Upon addition of water to the filtrate, an amorphous yellow solid precipitated. It was dried over phosphorus pentoxide at 100° and 0.1 mm. for two hours and recrystallized from benzene and petroleum ether; m.p. 98-99°.

Anal. Calcd. for  $C_{15}H_{13}O_3$ : C, 76.21; H, 3.42%; MW, 236.2.

Found: C, 76.11; H, 3.39%; MW, 234.7.

*The Mono-2,4-dinitrophenylhydrazone of (XXI)*

A mixture of 0.2 gm. of (XVIII), 0.2 gm. of 2,4-dinitrophenylhydrazone and 5 ml. of glacial acetic acid was refluxed for one hour. The flask was cooled and dark reddish-brown flakes separated; m.p. 126-130°.

Anal. Calcd. for  $C_{21}H_{11}O_6N_4$ : N, 13.51%. Found: N, 13.40%.

*Dibenz[a, c][1,3]cycloheptadiene (II)*

A mixture of 2.2 gm. of (I), 5 gm. of amalgamated zinc granules, and 15 ml. of glacial acetic acid containing 5 ml. of concentrated hydrochloric acid was refluxed for four hours with addition of 1 ml. of the acid each hour. The reaction mixture was made alkaline with 20% sodium hydroxide solution. The solution was evaporated to dryness on a steam bath. The residue was extracted with ether. The ether solution was evaporated and a residue was dissolved in glacial acetic acid. The solution was decolorized with carbon, hot filtrated, and titrated with water to turbidity. After the solution had been allowed to cool very slowly and to stand for one day a colorless, hairlike crystalline substance formed, m.p. 53-56°. The reported melting point of (II) is 54.5-55° (23).

Anal. Calcd. for  $C_{15}H_{14}$ : C, 92.75; H, 7.25%. Found: C, 92.01; H, 7.19%.

*6-Bromodibenz[a, c][1,3]cycloheptadiene-5,7-dione*

Bromine water was added to the solution of (I) in dilute sulphuric acid until the bromine color persisted for one minute. The solution was extracted with ether and the extract dried over anhydrous magnesium sulphate. A subsequent treatment of the ether solution with petroleum ether caused the precipitation of a pale yellow solid which after recrystallization from benzene and petroleum ether melted at 115-116°.

Anal. Calcd. for  $C_{15}H_9O_2Br$ : Br, 26.55%. Found: Br, 26.17%.

*6,6-Dibromo-dibenz[a, c][1,3]cycloheptadiene-5,7-dione*

A solution of 2.2 gm. of (I) and 10 ml. of chloroform was cooled in an ice bath and a solution of 1.7 gm. of dry bromine in 50 ml. of chloroform was added slowly during a period of 15 min. at 10° with stirring. The reaction was allowed to continue for 15 min. after all the bromine was added. The solvent was evaporated under reduced pressure at room temperature. The residue was recrystallized from benzene and petroleum ether. Light yellow crystals, m.p. 86-87°.

Anal. Calcd. for  $C_{15}H_8O_2Br_2$ : C, 47.19; H, 2.09; Br, 41.79%.

Found: C, 47.01; H, 2.11; Br, 42.53%.

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## NOTES

## 6,8-Dimethoxy-4-chromanone

A series of mono- and dimethoxy-4-chromanones were prepared during 1948-50 in this laboratory with the view of investigating the reactions of these compounds with the halogens. Table I gives those chromanones prepared, their oximes, and the parent mono- and dimethoxyphenoxypionic acids.

TABLE I  
MONO- AND DIMETHOXY-4-CHROMANONES

4-Chromanone			Oxime		Phenoxypionic Acid	
Substituent	M.p., °C.		M.p., °C.		M.p., °C.	
	Found	Lit.	Found	Lit.	Found	Lit.
None	37.5-38.5	38 (1) 38.5(11)	143-144	140(11) 144-145 (6)	94.5-95	97-98 (1)
6-Methoxy	44-45	49(10)	120.5-121	119(10)	109-110	110 (10)
7-Methoxy	56-57	56 (7) 58 (9)	136-138	137 (9)	81.5-82	82.5 (3) 82 (8)
8-Methoxy	87-88	89.5(10)	148-149	145-146(10)	133-133.5	135-136 (10)
5,7-Dime- thoxy	98	99 (2)	229-230		125-126	128-129 (2)
5,8-Dime- thoxy	117-118	113-115(13)	227-229		118-119	112-114(13)
6,7-Dime- thoxy	122-123	123-124 (2)	176.5-177.5		130-131	136-137 (2)
6,8-Dime- thoxy	101-102		169-170		101-102.5	
7,8-Dime- thoxy	99.5	101(10)	152	152-153(10)	99.5	101.5 (10)

The preparation of 6,8-dimethoxy-4-chromanone is given below. This compound is unreported in the chemical literature.

## EXPERIMENTAL

All melting points are uncorrected.

*2,4-Dimethoxyphenol* was obtained in 38% yield by oxidation of the Grignard reagent from bromoresorcinol dimethyl ether, according to the method of Gilman (4, 5) for 2,5-dimethoxyphenol; b.p. 129-131°C. at 11 mm. The benzoate, prepared by the Schotten-Baumann reaction, melted at 86-87°C.; literature (12), m.p. 90°C.

*$\beta$ -(2,4-Dimethoxyphenoxy)-propionic acid*.—2,4-Dimethoxyphenol, 4.4 gm., was dissolved in a warm solution of 3.56 gm. of potassium hydroxide in 9.2 ml. of water. The solution was cooled to room temperature and 3.14 gm. of  $\beta$ -chloro-propionic acid was added. The mixture was heated at the boiling point for 15 min., cooled, neutralized with 10% sulphuric acid, and extracted with ether. From this extract was reclaimed 1.75 gm. of 2,4-dimethoxyphenol. The aqueous

layer, upon acidification with sulphuric acid, deposited 2.8 gm. of 2,4-dimethoxyphenoxypropionic acid, m.p. 101.5-102.5°C., out of water.

Calc. for  $C_{11}H_{14}O_5$ :  $CH_3O$ , 27.4%. Found:  $CH_3O$ , 27.3%.

6,8-Dimethoxy-4-chromanone was prepared by heating for three hours under reflux with continuous stirring 2.1 gm. of 2,4-dimethoxyphenoxypropionic acid with 10 gm. of phosphoric anhydride in 75 ml. of dry benzene. The benzene was decanted, the residue treated with ice and water, then extracted with benzene. The combined benzene solutions were washed with dilute alkali and water, and dried with sodium sulphate. Removal of the benzene with a stream of nitrogen left a sticky yellow solid. Two crystallizations out of cyclohexane yielded 0.30 gm. of colorless 6,8-dimethoxychromanone, m.p. 101-102°C. Calc. for  $C_{11}H_{12}O_4$ : C, 63.5; H, 5.77%. Found: C, 63.2; H, 6.00%. The oxime, white needles from 50% ethanol, melted at 169-170°C.

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#### Urea Derivatives<sup>1</sup>

A series of urea derivatives were prepared for the purpose of examining their physical properties. The new ones are recorded in Table I along with their melting points. In addition the cyclic ureas (2-imidazolidones) 1-β-hydroxyethyl-2-imidazolidone and 1,2-bis-1-(2-imidazolidonyl)ethane were prepared. These last two compounds on nitration in acetic anhydride-nitric acid medium gave 1-β-nitroxyethyl-3-nitro-2-imidazolidone and 1,2-bis-1-(3-nitro-2-imidazolidonyl)ethane which proved to be identical with the hydrolysis products (2) from 1-β-nitroxyethyl-2-nitrimino-3-nitroimidazolidine and 1,2-bis-1-(2-nitrimino-3-nitroimidazolidinyl)ethane respectively. This, together with the ultraviolet studies (3), confirms the structures assigned to the 1-substituted-2-nitrimino-3-nitroimidazolidines (2).

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EXPERIMENTAL<sup>2,3</sup>*Isocyanates*

*p*-Tolylisocyanate, *p*-anisylisocyanate, and *p*-phenetylisocyanate were obtained from Eastman Kodak, Rochester, N.Y.

*Benzylisocyanate*

Benzylisocyanate (b.p.<sub>17</sub> 103°C.) was prepared in 46% yield as previously described (1).

*Ethylisocyanate*

Ethylisocyanate (b.p.<sub>760</sub> 59.5-60°C.) was prepared in 87% yield by the method of Slotta and Lorenz (4).

*Urea Derivatives*

The isocyanates (0.027 mole) were added to an amine (0.025 mole) dissolved in 30-35 cc. of benzene with cooling when necessary. The corresponding ureas crystallized from the benzene solution almost immediately. Occasionally it was necessary to add petroleum ether (b.p. 30-60°C.) to the benzene solution to complete precipitation of the urea derivative. The urea derivatives were obtained in practically quantitative yields and they melted 1-5° below the purified melting point. They were purified readily by crystallization from 95% ethanol or glacial acetic acid. The hitherto unreported urea derivatives are listed in Table I with their melting points.

*1-β-Hydroxyethyl-2-imidazolidone*

1-β-Hydroxyethyl-2-imidazolidone (m.p. 58-59°C.) was obtained in 50% yield from urea and 1-hydroxy-5-amino-3-azapentane employing the method of Wilson (5). Wilson reported the melting point as 50-51°C.

Calc. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 46.15; H, 7.69; N, 21.54%. Found: C, 45.91; H, 7.71; N, 21.30%.

*1,2-bis-1-(2-Imidazolidonyl)ethane*

Urea (10 gm., 0.165 mole) and 1,8-diamino-3,6-diazaoctane (17.9 gm., 0.124 mole) were heated together at 150-190°C. until ammonia evolution ceased. The cooled reaction mixture was washed with methanol (200 cc.) to give 12.97 gm. (75.1%) of 1,2-bis-1-(2-imidazolidonyl)ethane melting at 248-252.5°C. One crystallization from water (29 cc.) raised the melting point to 253.5-254.5°C. The melting point previously reported (5) is 240-245°C. Calc. for C<sub>8</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 48.49; H, 7.07; N, 28.28%. Found: C, 48.18; H, 7.40; N, 28.00%.

*1-β-Nitroxyethyl-3-nitro-2-imidazolidone*

Two grams (0.0154 mole) of 1-β-hydroxyethyl-2-imidazolidone were added to a solution of 6.3 cc. (0.15 mole) of absolute nitric acid in 14.45 cc. (0.15 mole) of acetic anhydride at 0°C. The temperature was allowed to rise to room temperature during the course of 40 min. Then the solution was poured onto ice with stirring. After the solution had stood in an open beaker for three days, a crop of crystals (m.p. 102-103°C.) was obtained, yield 1.66 gm. (49%). This material on admixture with a sample of 1-β-nitroxyethyl-3-nitro-2-imidazolidone (m.p. 102-103°C.) from the hydrolysis of 1-β-nitroxyethyl-2-nitrimino-3-nitro-imidazolidine (2) did not depress the melting point.

*1,2-bis-1-(3-Nitro-2-imidazolidonyl)ethane*

1,2-bis-1-(2-Imidazolidonyl)ethane 2 gm. (0.01 mole) was added to a solution

<sup>2</sup> All melting points were determined on a Kofler block.

<sup>3</sup> Microanalyses by Mr. C. W. Beasley, Skokie, Ill.



TABLE I  
RNHCONHR'

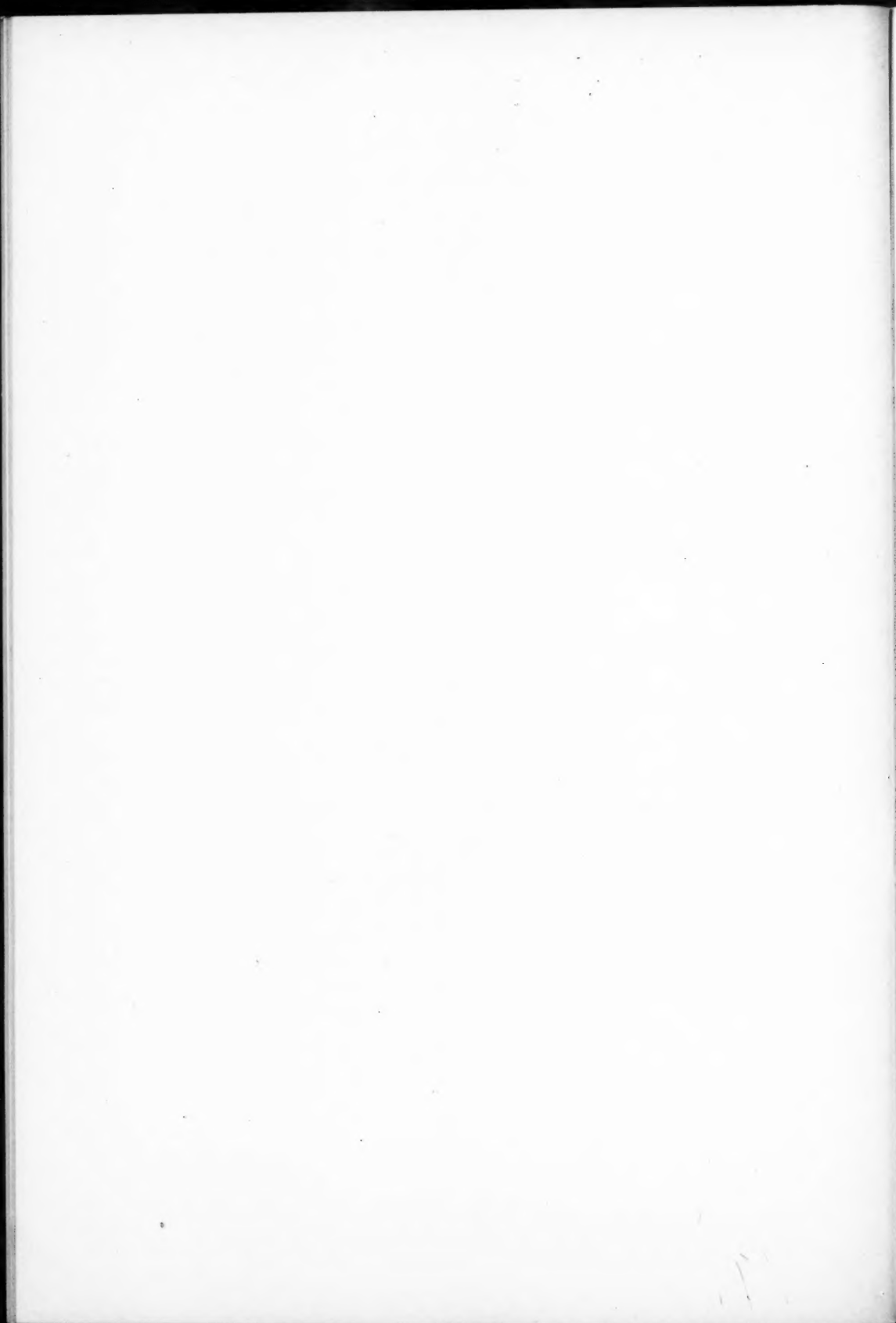
R	R'	M.p., °C.	N		Halogen	
			Calcd.	Found	Calcd.	Found
Benzyl	<i>p</i> -Phenetyl	181.5-182	10.35	10.13		
Benzyl	<i>p</i> -Chlorophenyl	207.5-208.5			13.61	13.93
Benzyl	<i>p</i> -Bromophenyl	222.5-223			26.40	25.95
Benzyl	<i>o</i> -Bromophenyl	168-168.5	9.15	9.03		
Ethyl	<i>m</i> -Tolyl	99.5-100.5	15.73	15.72		
Ethyl	<i>o</i> -Bromophenyl	148-148.5			32.90	32.45
Ethyl	<i>o</i> -Anisyl	141.5-142	14.44	14.31		
Ethyl	$\beta$ -Phenylethyl	77-78	14.58	14.36		
<i>p</i> -Tolyl	<i>p</i> -Phenetyl	215.5-216.5	10.37	10.60		
<i>p</i> -Tolyl	<i>m</i> -Phenetyl	179-180	10.37	10.43		
<i>p</i> -Tolyl	<i>o</i> -Phenetyl	175.5-176.3	10.37	10.57		
<i>p</i> -Tolyl	<i>p</i> -Anisyl	240-240.5	10.94	11.00		
<i>p</i> -Tolyl	<i>m</i> -Anisyl	189-189.5	10.94	11.08		
<i>p</i> -Tolyl	<i>o</i> -Anisyl	157.5-158	10.94	10.96		
<i>p</i> -Tolyl	<i>m</i> -Tolyl	209-209.2	11.66	11.96		
<i>p</i> -Tolyl	<i>o</i> -Chlorophenyl	211.5-212	10.74	11.00		
<i>p</i> -Tolyl	<i>o</i> -Bromophenyl	223.5-224			26.23	26.30
<i>p</i> -Anisyl	<i>p</i> -Phenetyl	215.5-216	9.79	9.80		
<i>p</i> -Anisyl	<i>m</i> -Phenetyl	165-165.5	9.79	9.78		
<i>p</i> -Anisyl	<i>o</i> -Phenetyl	137.2-137.8	9.79	10.06		
<i>p</i> -Anisyl	<i>m</i> -Anisyl	158-158.2	10.29	10.27		
<i>p</i> -Anisyl	<i>o</i> -Anisyl	145.5-145.8	10.29	10.35		
<i>p</i> -Anisyl	<i>m</i> -Tolyl	189-189.4	11.14	11.24		
<i>p</i> -Anisyl	<i>o</i> -Tolyl	203.5-204.5	11.14	11.05		
<i>p</i> -Anisyl	<i>p</i> -Chlorophenyl	271-271.5	10.13	10.42		
<i>p</i> -Anisyl	<i>m</i> -Chlorophenyl	202-202.2	10.13	10.13		
<i>p</i> -Anisyl	<i>o</i> -Chlorophenyl	193-193.2	10.13	10.20		
<i>p</i> -Anisyl	<i>m</i> -Bromophenyl	204.5-205			24.92	24.30
<i>p</i> -Anisyl	<i>o</i> -Bromophenyl	199-199.5			24.92	25.30
<i>p</i> -Phenetyl	<i>m</i> -Phenetyl	160-160.3	9.33	9.55		
<i>p</i> -Phenetyl	<i>o</i> -Phenetyl	147.5-148	9.33	9.76		
<i>p</i> -Phenetyl	<i>o</i> -Anisyl	162-162.5	9.79	10.06		
<i>p</i> -Phenetyl	<i>m</i> -Tolyl	169.5-170	10.37	10.68		
<i>p</i> -Phenetyl	<i>o</i> -Tolyl	210	10.37	10.70		
<i>p</i> -Phenetyl	<i>p</i> -Chlorophenyl	246.7			12.22	12.60
<i>p</i> -Phenetyl	<i>m</i> -Chlorophenyl	199.2-199.5			12.22	12.46
<i>p</i> -Phenetyl	<i>o</i> -Chlorophenyl	182.2-182.8			12.22	12.46
<i>p</i> -Phenetyl	<i>m</i> -Bromophenyl	197-197.5			23.88	23.83
<i>p</i> -Phenetyl	<i>o</i> -Bromophenyl	189-189.2			23.88	24.46

of 4.19 cc. (0.10 mole) of absolute nitric acid in 9.7 cc. (0.10 mole) of acetic anhydride at 0°C. The temperature was raised to 22°C. and maintained at this level for 30 min. Then the reaction mixture was poured onto ice and the precipitate recovered by filtration. The product melted at 241-243°C. with decomposition, yield 2.35 gm. (78.5%). It did not depress the melting point of 1,2-*bis*-1-(3-nitro-2-imidazolidonyl)ethane (m.p. 242-243°C. with decomposition) obtained from the hydrolysis of 1,2-*bis*-1-(2-nitrimino-3-nitroimidazolidinyl)ethane (2).

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